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Syntheses and Properties of Trifluoromethanesulfonyloxy Derivatives of Tricyclohexylphosphine–Borane

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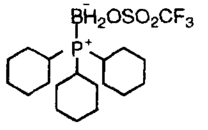
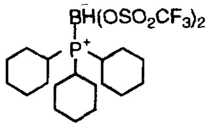
Abstract: Syntheses, structural characterizations, and reactions of tricyclohexylphosphine–trifluoromethanesulfonyloxyborane and tricyclohexylphosphine–bis(trifluoromethanesulfonyloxy)-borane are described.

In our continuing study on phosphine–boranes,[1] we found that phosphine–boranes possessing a methanesulfonyloxy group at the boron atom were subjected to nucleophilic substitution reaction with sulfur or phosphorus nucleophiles.[2] Based on these results, we have tried to synthesize trifluoromethanesulfonyloxy derivatives of phosphine–boranes, anticipating that they might exhibit exceedingly high reactivities in this class of compounds and might have potential utility as the precursors of boron-functionalized phosphine–boranes. Here we report syntheses, structural characterizations, and reactions of tricyclohexylphosphine–trifluoromethanesulfonyloxyborane (**1**) and tricyclohexylphosphine–bis(trifluoromethanesulfonyloxy)borane (**2**).

Compound **1** was synthesized by the treatment of tricyclohexylphosphine–borane with 1.2 equivalents of trifluoromethanesulfonic acid in benzene.[3] When tricyclohexylphosphine–borane was treated with 2.4 equivalents of trifluoromethanesulfonic acid, compound **2** was obtained in 72 % yield after recrystallization from cyclohexane.[4] The structures of these compounds were unequivocally determined by single crystal X-ray analyses.[5–7] The ORTEP drawings are shown in Figs. 1 and 2.



1



2

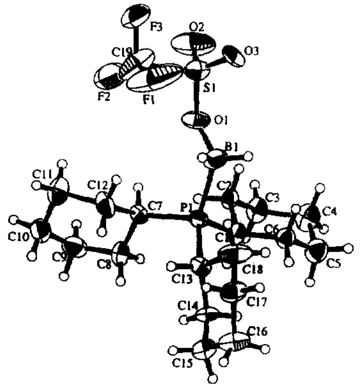


Fig. 1. An ORTEP drawing of one of the two crystallographically independent molecules of compound **1**

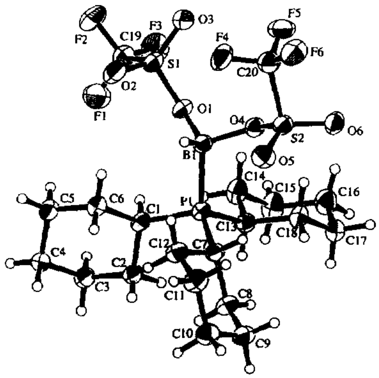


Fig. 2. An ORTEP drawing of compound **2**

Table 1. The reactions of compound **1** with nucleophiles

Reagent	Conditions[a]	Product[b]	Mp (°C)	Yield/%[c]
$LiAlD_4$	0 °C, 0.5 h	Cy_3PBH_2D	175–177	86
$CeCl_3$	50 °C, 5 h	Cy_3PBH_2Cl	163–164	89
LiBr	rt, 0.5 h	Cy_3PBH_2Br	137–139	88
LiCN	rt, 1 h	Cy_3PBH_2CN	174–176	45
PhSH/NaH	0 °C, 0.5 h	Cy_3PBH_2SPh	101–103	82
$Me_3SiC\equiv CLi$	rt, 6 h	$Cy_3PBH_2C\equiv CSiMe_3$	136–137	81
$(CH_3)_2Cu(CN)Li_2$	rt, 2 h[e]	$Cy_3PBH_2CH_3$	115–116	28[f]
$(n\text{-}C_4H_9)_2Cu(CN)Li_2$	–20 °C, 1 h, 0 °C, 0.5 h	$Cy_3PBH_2C_4H_9\text{-}n$	84–85	78
$(s\text{-}C_4H_9)_2Cu(CN)Li_2$	–30 °C, 2 h, 0 °C, 0.5 h	$Cy_3PBH_2C_4H_9\text{-}s$	90–91	89

[a] All reactions were carried out in THF using 1 mmol of compound 1 and 2 mmol of the reagent unless otherwise stated. [b] All compounds synthesized afforded satisfactory spectral data and elemental analyses (C, H, N). [c] Isolated yields. [d] In dimethylformamide. [e] In THF–ether (2 : 1). [f] Tricyclohexylphosphine–borane was produced in 25% yield.

The reactivities of compounds **1** and **2** were examined. These compounds rapidly decomposed on contact with water to give tricycohexylphosphine after treatment with aqueous potassium carbonate.[8] Compound **1** reacted readily with various nucleophiles to give the corresponding substitution products (Table 1).[9] It is noted that *B*-alkylation products were obtained by the use of higher-order organocuprates.[10]

References and Notes

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3. Trifluoromethanesulfonic acid (0.53 mL, 6 mmol) was added during 5 min to a solution of tricyclohexylphosphine–borane (1.47 g, 5 mmol) in dry benzene (25 mL) at room temperature. After hydrogen evolution subsided, the solution was stirred with powdered potassium hydrogencarbonate (300 mg) and filtered under argon. The filtrate was evaporated under reduced pressure, and the residual solid was recrystallized twice from dry hexane under argon to give colorless crystals (1.54 g, 68%). Mp 139–142 °C (decomp.) (hexane); ^1H NMR ($CDCl_3$) δ 1.2–2.3 (m, 33H); IR (KBr) 2425, 2390 cm^{-1}; MS (FAB): 441 (M–1, 4), 280 (72), 198 (100). Anal. Calcd for $C_{19}H_{35}BF_3O_3PS$: C, 51.59; H, 7.98. Found: C, 51.72; H, 8.00.
4. Compound **2**: mp ca. 175 °C (decomp.) (cyclohexane); ^1H NMR ($CDCl_3$) δ 1.2–2.3 (33H); IR (KBr) 2510 cm^{-1}; MS (FAB) 589 (M–1, 7), 441 (100), 281 (76). Anal. Calcd for $C_{20}H_{34}BF_6O_6PS_2$: C, 40.69; H, 5.81. Found: C, 40.78; H, 5.78.
5. The two dimensional IP detector on RIGAKU R-AXIS IIC was used for rapid analysis for both compounds **1** and **2**.
6. The crystals for the X-ray analysis were obtained by recrystallization from hexane. X-ray crystallographic data for compound **1**: $C_{19}H_{35}BF_3O_3PS$, FW = 442.32, monoclinic, $P2_1$, $a = 10.167(6)$, $b = 19.185(3)$, $c = 11.825(3)$Å, $\beta = 98.30(3)°$, $V = 2282(1)$Å^3, $Z = 4$ (two molecules in asymmetric unit), $D_{calc} = 1.287$ g cm^{-3}, temperature of data collection: 296K, 3702 unique reflections ($I > 4.50\sigma(I)$), $R = 0.095$, $R_W = 0.102$. Selected bond lengths (Å) and angles (deg): P–B 1.95(3), B–O1 1.54(4), P–C1 1.85(3), P–C7 1.82(2), P–C13 1.90(2), P–B–O1 105(1), B–P–C1 115(1), B–P–C7 109(1), B–P–C13 107(1), C1–P–C7 106(1), C7–P–C13 107.4(10), C13–P–C1 111.1(10). Full details of the structure determination have been deposited at the Cambridge Crystallographic Centre.
7. The crystals for X-ray analysis were obtained by recrystallization from hexane. X-ray crystallographic data for compound **2**: $C_{20}H_{34}BF_6O_6PS_2$, FW = 590.38, prismatic, triclinic $P\bar{1}$, $a = 9.872(8)$, $b = 14.24(2)$, $c = 9.72(1)$Å, $\alpha = 102.9(1)$, $\beta = 97.81(6)$, $\gamma = 92.58(9)°$, $V = 1315(3)$Å^3, $Z = 2$, $D_{calc} = 1.487$ g cm^{-3}, temperature of data collection: 173K, 2537 unique reflections ($I > 3.00\sigma(I)$), $R = 0.066$, $R_W = 0.081$. Selected bond lengths (Å) and angles (deg): P–B 1.961(6), B–O1 1.500(6), B–O4 1.506(6), P–C1 1.837(5), P–C7 1.823(5), P–C13 1.829(5), P–B–O1 108.5(3), P–B–O4 109.6(3), O1–B–O4 105.0(4), B–P–C1 108.3(2), B–P–C7 106.4(2), B–P–C13 114.2(2), C1–P–C7 114.4(2), C7–P–C13 107.6(2), C1–P–C13 106.1(2). Full details of the structure determination have been deposited at the Cambridge Crystallographic Centre.
8. McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.
9. Compound **2** reacted with $LiAlD_4$ in THF at 0 °C to give $(C_6H_{11})_3PBHD_2$ in excellent yield. However, the reactions with LiCN, PhSNa, or $(n\text{-}C_4H_9)_2Cu(CN)Li_2$ resulted in the formation of complex mixtures.
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