1D2b

Synthesis and Structural Comparison of Boron Compounds Bearing Various Tridentate Ligands

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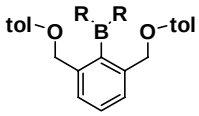
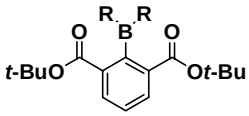
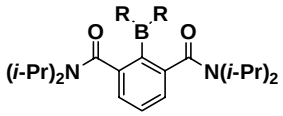
Recently we reported synthesis and crystal structures of hypervalent carbon species using a flexible tridentate ligand composed of 2,6-bis(*p*-substituted phenoxymethyl)benzene[1]. In the series, probably due to the flexibility of the tridentate ligand, a large structural diversity depending upon the substituents on the central carbon atom was observed. In order to examine differences in structure due to electronic nature of the oxygen ligands and the substituents on the central atom, several organoboron compounds having a family of tridentate ligands based on 2,6-bis(*p*-tolyloxymethyl) benzene (**1a-c**)[2], di-*tert*-butyl isophthalate (**2a-c**), and *N*,*N*,*N*',*N*'-tetraisopropyl-isophthalamide (**3a-b**) were prepared and crystallographically analyzed (**Table 1**). Comparing pentacoordinated species (**1b**, **1c**, **2a**, and **2b**), the stronger donating ability of the oxygen atoms and the more electrophilic boron atom prefer the stronger B–O interactions.



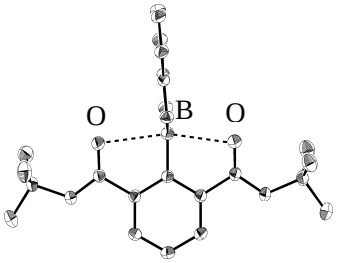
1a : R = pinacol
1b : R = catechol
1c : R = phenyl



2a : R = pinacol
2b : R = catechol
2c : R = fluorenyl



3a : R = pinacol
3b : R = catechol



Ortep drawing of **2b**

Table 1 Comparison of B-O distance (Å) of boron compounds **1-3**

Substituent		Donicity Strength of Oxygen Atoms →		
		ether	ester	amide
Electrophilicity of Boron Atom ↓	pinacol	3.024(3), 3.155(3) **1a** : tricoordinate	2.524(2), 2.570(2) **2a** : **pentacoordinate**	3.427(4), 3.478(5) **3a** : tricoordinate
	catechol	2.528(9), 2.660(9) 2.496(9), 2.703(10) **1b** : **pentacoordinate**	2.458(2), 2.560(2) **2b** : **pentacoordinate**	1.561(4), 3.770(5) **3b** : tetracoordinate
	diaryl	2.561(3), 2.749(4) 2.539(3), 2.752(4) **1c** : **pentacoordinate**	1.638(5), 3.110(5) **2c** : tetracoordinate	

1) Akiba, K.-y.; Moriyama, Y.; Mizozoe, M.; Inohara, H.; Nishii, T.; Yamamoto, Y.; Minoura, M.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Ishimura, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 5893.

2) Nakatsuji, J.-y.; Moriyama, Y.; Matsukawa, S.; Yamamoto, Y.; Akiba, K.-y. *Main Group Chem.*, **2006**, *5(4)*, 277.