

Defining the Conformation of Lewis Acid/Lewis Base Complexes: Crystallographic Evidence for Simultaneous σ and π Donation by a Carbonyl Group to a Divalent Boron Lewis Acid**

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Because Lewis acids are extraordinarily versatile catalysts,^[1] a great deal of effort has been devoted to the development of *chiral* Lewis acid catalysts.^[2, 3] Defining the conformation about the dative bond between substrate and Lewis acid is one of the important issues faced in the design of an effective catalyst (for example, see A).^[4, 5] Several successful strategies

for restricting this rotational degree of freedom, typically through a two-point interaction between reactant and catalyst, have been described.^[6, 7]

Our approach to addressing this conformational issue focuses on the development of Lewis acids that bear both an empty σ -symmetry and an empty π -symmetry orbital (Figure 1). These

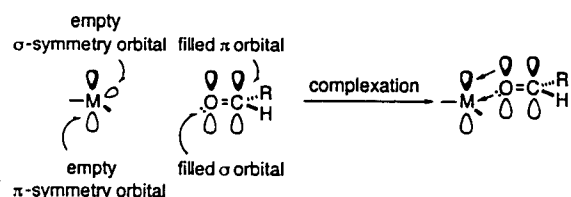


Figure 1. Simultaneous σ and π donation by a carbonyl group to a divalent Lewis acid.

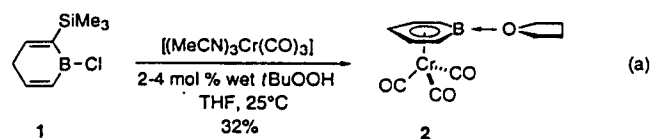
vacant orbitals can simultaneously accept electron density from an oxygen lone pair and from the π system of a carbonyl group.^[8] The distinguishing feature of this approach is the π -symmetry interaction, which at once organizes the donor-acceptor complex and activates the substrate toward nucleophilic addition.^[9] In this report we provide structural data^[10] that suggests that a π interaction of the type illustrated in Figure 1 can indeed define the conformation of a complex formed between a carbonyl compound and a Lewis acid.

The $[(\eta^6\text{-borabenzene})\text{Cr}(\text{CO})_3]$ framework (B) seemed well-suited for our initial studies, since the divalent boron atom bears both an empty σ -symmetry orbital and an empty, relatively low-lying π -symmetry orbital, the π^* orbital of the aromatic ring;^[11, 12] complexing borabenzene to $\text{Cr}(\text{CO})_3$, a powerful electron-withdrawing group, should significantly lower the energy of the π^* orbital of $[(\eta^6\text{-borabenzene})\text{Cr}(\text{CO})_3]$

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below that of borabenzene itself.^[13] Treatment of boracycle 1^[14] with $[(\text{MeCN})_3\text{Cr}(\text{CO})_3]$ in THF affords air- and moisture-sensitive $[(\eta^6\text{-borabenzene-THF})\text{Cr}(\text{CO})_3]$ (2) [Eq. (a)].^[15] An



X-ray diffraction study of 2 reveals that the THF binds to the boron atom with a slightly distorted trigonal-planar geometry at oxygen ($\angle \text{B-O4-C4} + \angle \text{B-O4-C7} + \angle \text{C4-O4-C7} = 356^\circ$; Figure 2 top and Table 1).^[16] The B-O bond in 2 (1.467 Å) is

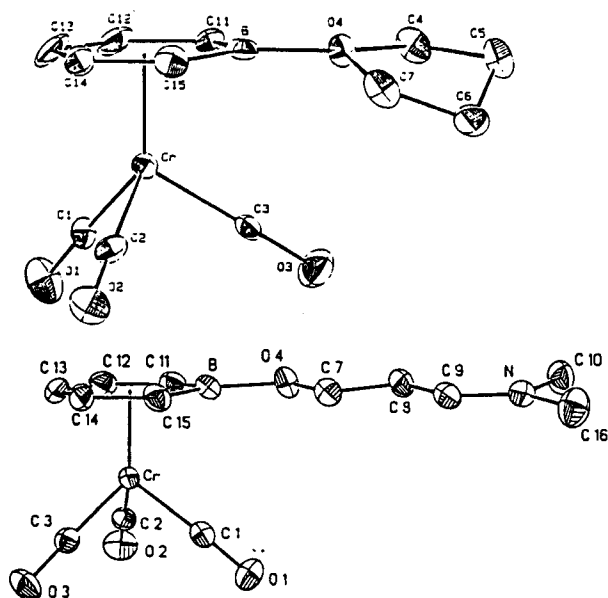


Figure 2. X-ray structure analyses of 2 (top) and 3 (bottom); ORTEP representations with thermal ellipsoids drawn at the 35% probability level.

markedly shorter than that observed in any other boron-based THF complex (1.51–1.59 Å).^[17, 18] The structure is consistent with donation from a filled π -symmetry oxygen orbital to an empty π -symmetry borabenzene orbital.

Complex 2 reacts with 3-(dimethylamino)acrolein to provide $[(\eta^6\text{-borabenzene-3-(dimethylamino)acrolein})\text{Cr}(\text{CO})_3]$ (3) [Eq. (b)].^[19] The crystal structure of 3 (Figure 2 bottom,

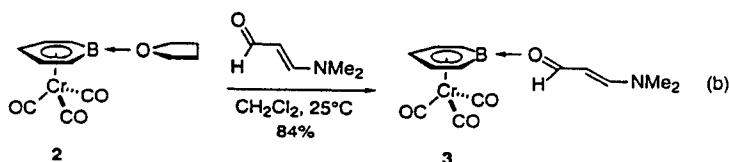


Table 1)^[20, 21] displays the following features, each of which is typical for Lewis acid/aldehyde complexes:^[4] 1) the Lewis-acidic atom lies in the plane of the carbonyl group ($\angle \text{B-O4-C7-C8} = -176^\circ$); 2) the Lewis acid binds *syn* to the hydrogen of the aldehyde, rather than *syn* to the carbon substituent;^[22, 23] and 3) the Lewis acid-oxygen-carbon angle is roughly 120° ($\angle \text{B-O4-C7} = 123^\circ$).

Table 1. Selected bond lengths [Å], bond angles [°], and torsion angles [°] for 2 and 3.

Parameter	2	3
B-O4	1.467(8)	1.451(5)
B-C11	1.48(1)	1.490(6)
C11-C12	1.407(9)	1.411(6)
C12-C13	1.41(1)	1.397(6)
C13-C14	1.395(9)	1.407(6)
C14-C15	1.407(8)	1.399(5)
C(15)-B	1.50(1)	1.508(6)
Cr-C1	1.816(7)	1.821(4)
Cr-C2	1.853(7)	1.816(4)
Cr-C3	1.808(6)	1.808(4)
C1-O1	1.155(7)	1.166(5)
C2-O2	1.151(7)	1.169(5)
C3-O3	1.175(6)	1.170(4)
O4-C7	-	1.316(4)
C7-C8	-	1.345(5)
C8-C9	-	1.400(5)
C9-N	-	1.291(4)
N-C10	-	1.466(5)
N-C16	-	1.465(5)
C11-B-O4	120.3(7)	118.1(3)
C15-B-O4	121.2(7)	125.7(3)
B-O4-C7	124.2(5)	122.9(3)
B-O4-C4	123.2(6)	-
C4-O4-C7	109.1(5)	-
C11-C12-C13	121.3(7)	121.4(4)
C12-C13-C14	121.2(7)	120.9(4)
C13-C14-C15	122.0(7)	122.0(4)
C14-C15-B	118.1(7)	119.3(4)
C15-B-C11	118.4(6)	116.2(3)
B-C11-C12	119.0(7)	120.0(4)
O4-C7-C8	-	122.4(3)
C7-C8-C9	-	119.1(3)
C8-C9-N	-	126.8(3)
C9-N-C10	-	122.1(3)
C9-N-C16	-	122.2(3)
C10-N-C16	-	115.8(3)
O4-B-C11-C12	179.1(6) [a]	176.68(33)
O4-B-C15-C14	-179.4(6)	-176.59(34)
C4-O4-B-C11	-1(1)	-
C4-O4-B-C15	175.0(6)	-
C7-O4-B-C11	-157.7(6)	-173.12(33)
C7-O4-B-C15	18.4(9)	4.63(56)
B-O4-C7-C8	-	-175.59(34)
O4-C7-C8-C9	-	-179.38(32)
C7-C8-C9-N	-	175.49(35)
C10-N-C9-C8	-	-0.28(56)
C16-N-C9-C8	-	178.89(35)

[a] The sign of the torsion angle is positive if, when on looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

Table 2. Bond lengths [Å] in bound and free 3-aminoacroleins.

Parameter	3	free 3-aminoacrolein
B-O	1.451(5)	-
C=O	1.316(4)	1.23
C _{carbonyl} -C _α	1.345(5)	1.41

NMR data are also indicative of a strong interaction between the Lewis acid and the Lewis base components of adduct 3. As illustrated in Figure 3, the ¹H and ¹³C NMR resonances of 3-(dimethylamino)acrolein are shifted significantly downfield upon binding to boron.^[28-30]

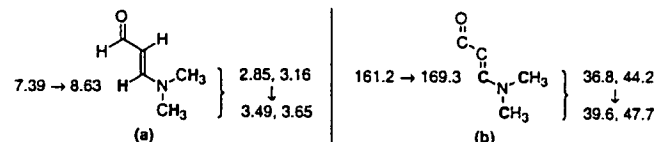


Figure 3. NMR chemical shifts [δ] of 3-(dimethylamino)acrolein and complex 3. a) ¹H NMR data (free → complexed aldehyde); b) ¹³C NMR data (free → complexed aldehyde).

This structural study provides the first experimental support for the suggestion that donation of electron density simultaneously by a lone pair and by the π system of a carbonyl group to a Lewis acid can organize the resulting complex.^[31] In contrast to some of the previous strategies for defining the conformation of Lewis acid/Lewis base adducts, this approach does not require a two-point interaction between the two components. Our current efforts are directed toward developing chiral catalysts based on the [(η⁶-borabenzene)Cr(CO)₃] framework.

Experimental Section

Reactions were carried out under an atmosphere of nitrogen in oven-dried glassware inside a Vacuum Atmospheres HE-43-2 glove box.

2: This reaction is sensitive to the amount of wet *t*BuOOH used, and the optimum stoichiometry varies with the batch of boracycle 1. Therefore, to determine the appropriate stoichiometry of wet *t*BuOOH to employ for a given batch of 1, three reactions were routinely set up side-by-side, wherein *t*BuOOH (1.0 μL, 2.0 μL, or 3.0 μL; 70% in H₂O) was added to a solution of boracycle 1 (50 mg, 0.27 mmol) in 1.5 mL of THF at room temperature. The resulting solutions were immediately added to vials containing [(MeCN)₃Cr(CO)₃] (70 mg, 0.27 mmol). The vials were then capped and shaken vigorously until most of the [(MeCN)₃Cr(CO)₃] had dissolved (ca. 2 min). The reaction mixtures were allowed to stand at room temperature for 10 min (during which time the yellow product may begin to precipitate), and then they were cooled to -35 °C. (If too little (dark purple-brown reaction mixture) or too much (yellow-orange reaction mixture) *t*BuOOH was present, then no product precipitated from solution; a successful reaction maintained a yellow-brown color, from which complex 2 precipitated as a yellow-brown solid.) The supernatant of the successful reaction was removed by pipet, and unreacted [(MeCN)₃Cr(CO)₃] was removed by washing the remaining solid with Et₂O until the washings were colorless. The resulting yellow-brown solid turned yellow upon washing with THF (3 × 1 mL). The Et₂O and THF washings were added to the supernatant and cooled to -35 °C, thereby providing a second crop of crystals. Combining the two crops afforded THF adduct 2 in 30% yield. Once the optimum stoichiometry of wet *t*BuOOH had been determined by this procedure, the successful reaction could be scaled up; scaling this process up by a factor of four reproducibly furnished 2 in 30–35% yield. ¹H NMR (300 MHz, CD₂Cl₂): δ = 5.57 (approx. t, 2H, *J* = 7.2 Hz), 4.94 (t, 1H, *J* = 6 Hz), 4.88–4.84 (br. m, 4H), 3.91 (d, 2H, *J* = 9.9 Hz), 2.43–2.39 (br. m, 4H); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 238.0, 105.5, 84.0, 80.2, 77 (br.), 25.6; ¹¹B NMR (96 MHz, CD₂Cl₂): δ = 28.5; FTIR (THF): ν̄ [cm⁻¹] = 2926, 2681, 1967, 1932, 1846, 1829, 1460; HRMS calcd for C₁₂H₁₃BCrO₄: 284.0312; found: 284.0311.

3: Neat 3-(dimethylamino)acrolein (65 mg, 0.66 mmol) was added to a solution of 2 (50 mg, 0.18 mmol) in 2.0 mL of CH₂Cl₂ at room temperature. After standing for 10 min at room temperature, the solution was cooled to -35 °C overnight, during which time 3 crystallized as orange microcrystals. The supernatant was decanted, and the solid was washed with hexane and then dried, affording 57 mg (84%) of

pure 3. Compound 3 decomposes at -35°C over a period of months. $^1\text{H NMR}$ (300 MHz, $[\text{D}_2]\text{DMF}$): $\delta = 8.63$ (d, 1H, $J = 6.9$ Hz), 8.46 (d, 1H, $J = 6.6$ Hz), 6.39 (approx. t, 1H, $J = 6.6$ Hz), 5.34 (dd, 2H, $J = 5.4, 3.6$ Hz), 4.86 (t, 1H, $J = 3.6$ Hz), 3.89 (d, 2H, $J = 5.1$ Hz), 3.65 (s, 3H), 3.49 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, $[\text{D}_2]\text{DMF}$): $\delta = 239.1, 177.1, 169.3, 106.1, 103.3, 82.1, 80$ (br.), 47.7, 39.6; $^{11}\text{B NMR}$ (96 MHz, $[\text{D}_2]\text{DMF}$): $\delta = 28.8$; FTIR (CH_2Cl_2): $\tilde{\nu}$ (cm^{-1}): 1922, 1821, 1649, 1605; analysis calcd for $\text{C}_{11}\text{H}_{14}\text{BCrNO}_4$: C 50.15, H 4.54, N 4.50; found: C 50.13, H 4.55, N 4.36; HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{BCrNO}_4$: 311.0421; found: 311.0422.

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- [16] Crystal data for 2: Yellow prism (0.22 × 0.22 × 0.17 mm), orthorhombic, $Pbcu$, $a = 12.64(1)$, $b = 15.618(6)$, $c = 12.517(6)$ Å, $V = 2472(2)$ Å 3 , $Z = 8$, and $\rho_{\text{calc}} = 1.526$ g cm $^{-3}$. A Rigaku AFC6S diffractometer operating at $T = -86(1)^{\circ}\text{C}$ with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å) was used to collect ω -2 θ scans ($2\theta_{\text{max}} = 55.0^{\circ}$). The data consisted of 3215 unique reflections and was corrected for Lorentz polarization effects and absorption (DIFABS, $\mu(\text{MoK}\alpha) = 9.03$ cm $^{-1}$, transmission factors 0.91–1.12). Solution by direct methods and standard difference Fourier techniques, full-matrix least-squares refinement on F^2 (1005 data with $I > 3\sigma(I)$) were refined for 163 parameters in the last refinement cycle). $R_1 = 0.050$, $wR_2 = 0.037$, GOF = 1.58. Largest peak and hole: 0.38 and -0.33 e Å $^{-3}$. All non-hydrogen atoms were refined anisotropically; hydrogens were assigned to calculated positions and refined with an overall isotropic thermal parameter. All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corporation. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-132. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: Int. code + (1223) 336-0333; e-mail: deposit@chemcryst.cam.ac.uk).
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- [19] Preliminary data indicate that the conversion of 2 to 3 proceeds through an addition–elimination mechanism.
- [20] Crystal data for 3: Red-orange crystal (0.18 × 0.14 × 0.05 mm), triclinic, $P\bar{1}$, $a = 6.6231(7)$, $b = 10.6659(12)$, $c = 10.9415(12)$ Å, $\alpha = 107.937(2)$, $\beta = 92.506(2)$, $\gamma = 107.189(2)^{\circ}$, $V = 694.75(13)$ Å 3 , $Z = 2$, and $\rho_{\text{calc}} = 1.487$ g cm $^{-3}$. A Siemens SMART/CCD diffractometer operating at $T = -85(2)^{\circ}\text{C}$ with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) was used to collect ω scans ($1.98^{\circ} < \theta < 23.22^{\circ}$). The data consisted of 2803 total reflections, 1910 unique ($R_{\text{int}} = 0.0382$), and was corrected for Lorentz-polarization effects (but not for absorption). Solution by direct methods and standard difference Fourier techniques, full-matrix least-squares refinement on F^2 (1909 data with $I > 3\sigma(I)$) were refined for 181 parameters in the final cycle). $R_1 = 0.0400$, $wR_2 = 0.0990$ for all data with $I > 2\sigma(I)$ ($R_1 = 0.0433$; $wR_2 = 0.1052$ for all data). GOF = 1.207. Largest peak and hole: 0.533 and -0.366 e Å $^{-3}$. All non-hydrogen atoms were refined anisotropically; hydrogens were assigned to calculated positions and refined with an overall isotropic thermal parameter. The Siemens Software Package (SMART, SAINT, XPREP, SHELXTL) was used on a Silicon Graphics INDY workstation to handle all calculations.
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- [30] Our initial attempts to determine by NMR the barrier for rotation about the B–O bond have been unsuccessful.
- [31] Computational studies of borabenzene–aldehyde complexes are underway (Prof. M. DiMare, University of California, Santa Barbara, unpublished results).