Synthesis and characterization of new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O′,N]boranes

Teresa Mancilla,* Luis S. Zamudio-Rivera, Hiram, I. Beltrán, Rosa Santillan, and Norberto Farfán

Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,
Apartado postal 14-740, CP07000, México, D. F. MÉXICO.
E-mail: tmancill@cinvestav.mx

Dedicated to Professor Eusebio Juaristi on the occasion of his 55th birthday
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Abstract
The synthesis of nine (N→B) phenyl substituted[N-benzyliminodiacetate-O,O′,N]boranes 3a-3i is reported herein. These compounds were characterized by ¹H, ¹³C, ¹¹B, HETCOR, NOESY, infrared spectroscopy, mass spectrometry and in the case of compounds 3d and 3g also by ¹⁹F NMR. All compounds exhibit a bicyclic structure due to the presence of an intramolecular N→B coordination bond. The structure of 4-chlorophenyl[N-benzyliminodiacetate-O,O′,N]borane 3e was further established by a single crystal x-ray diffraction study. The correlation between δ¹¹B of compounds 3a, 3d-3i and σHammett values shows that the strength of the N→B bond depends on the electronic factors of the substituent on the B-phenyl group.

Keywords: Boranes, iminodiacetic acid, NMR, arylboranes and σHammett-

Introduction
There is considerable interest in boron heterocycles derived from aminoacids due to their potential use for biological studies. Cyclic boron compounds, mainly phenyl derivatives exhibit cytotoxic activity¹-⁵ and have application in boron neutron capture therapy (BNCT) for the treatment of brain tumors⁶,⁷ and melanomas⁸. We have been interested in the synthesis, characterization, structural analysis and reactivity of boron heterocycles derived from iminodiacetic acid and N-substituted imino- and aminodiacetic acids⁹-¹⁴. Herein, we describe the synthesis of nine new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O′,N]boranes, 3a-3i, where the phenyl group is substituted at the meta and para positions. Compounds 3a-3i were prepared by the reaction of N-benzyliminodiacetic acid 1 and phenyl substituted boronic acids 2a-2i in a 1:1 molar ratio (Scheme 1). All Compounds were characterized by ¹H, ¹³C, ¹¹B NMR,
HETCOR, NOESY, infrared spectroscopy and mass spectroscopy, in addition, for compounds 3d and 3g the $^{19}$F NMR spectra were also obtained.

**Results and Discussion**

The reaction of N-benzyliminodiacetic acid 1 with substituted phenylboronic acids 2a-2i in a 1:1 ratio, led to (N→B) phenyl substituted[N-benzyliminodiacetate-O,O’,N]boranes 3a-3i (Scheme 1). Compounds 3a-3i were obtained as white solids.

![Scheme 1](image)

**Scheme 1**

**NMR spectroscopy**

The $^1$H NMR spectra in DMSO-d$_6$ of compounds 3a-3i clearly show the AB coupling pattern for the diastereotopic H-2 protons, which evidences the presence of the intramolecular N→B coordination bond as has been observed for analogous compounds. The H-3 benzylic protons exhibit a single signal between 3.75 and 3.87 ppm (Table 1). The $^1$H NMR spectrum of compound 3d shows a doublet of doublets for H-9 and a triplet signal for H-10 due to coupling with $^{19}$F. The ($^1$H-$^1$H) NOESY spectra show correlation between H-2A and H-9 arom with H-3, which indicates that the H-2A protons are exo and H-9 is close to the H-3 benzylic protons.

The $\delta$ ($^{11}$B) values (Table 1) confirm the tetrahedral environment of the B nucleus, since they lie in the range reported previously for analogous boron heterocycles. Comparison of the $\delta$ ($^{11}$B) values for compounds 3a-3i with the unsubstituted (N→B) phenyl[N-benzyliminodiacetate-O,O’,N]borane [12.5 ppm], shows that: a) electron donating substituent at para position (3a) decrease the N→B coordination bond, while electron-withdrawing groups (3b, 3d-3f) strengthens this bond; b) electron-withdrawing groups at the meta position (3g-3i)
increase the N→B coordination bond. This shows that $\delta^{(11)}$B is sensitive to inductive and resonance factors and there should exist a correlation with $\sigma_{\text{Hammett}}$ values.\textsuperscript{22}

**Table 1.** $^1$H and $^{11}$B NMR data of 3a-3i: $\delta_H$ and $\delta_B$ [ppm] and coupling constants $J$ [Hz]

| Compound | H-2 | H-3 | C$_6$H$_5$ | B-C$_6$H$_4$R | $\delta^{(11)}$B |
|----------|-----|-----|-----------|---------------|----------------|
| 3a       | HA  | 4.40 | 16.9$^a$ | H-5 7.57-7-60 | H-9,13 7.48 7.7$^b$ |
|          | HB  | 3.91 | 16.9$^a$ | H-6,7 7.40-7.44 | H-10,12 7.23 7.7$^b$ |
|          |     |      |           |               | +12.9          |
| 3b       | HA  | 4.47 | 16.8$^a$ | H-5 7.58-7-60 | H-9,13 7.95 8.0$^b$ |
|          | HB  | 3.96 | 16.8$^a$ | H-6,7 7.40-7.42 | H-10,12 7.84 8.0$^b$ |
|          |     |      |           |               | +12.4          |
| 3c       | HA  | 4.35 | 16.8$^a$ | H-5 7.55-7-57 | H-9,13 7.50 8.4$^b$ |
|          | HB  | 3.86 | 16.8$^a$ | H-6,7 7.40-7.42 | H-10,12 6.97 8.4$^b$ |
|          |     |      |           |               | +12.0          |
| 3d       | HA  | 4.41 | 16.9$^a$ | H-5 7.55-7-60 | H-9,13 7.63 9.0$^b$ 6.4$^c$ |
|          | HB  | 3.91 | 16.9$^a$ | H-6,7 7.40-7.47 | H-10,12 7.24 9.0$^b$ |
|          |     |      |           |               | +12.2          |
| 3e       | HA  | 4.40 | 16.8$^a$ | H-5 7.56-7-58 | H-9,13 7.59 8.4$^b$ |
|          | HB  | 3.90 | 16.8$^a$ | H-6,7 7.39-7.43 | H-10,12 7.47 8.4$^b$ |
|          |     |      |           |               | +12.2          |
| 3f       | HA  | 4.40 | 16.8$^a$ | H-5 7.56-7-58 | H-9,13 7.61 8.0$^b$ |
|          | HB  | 3.90 | 16.8$^a$ | H-6,7 7.39-7.43 | H-10,12 7.53 8.0$^b$ |
|          |     |      |           |               | +12.1          |
| 3g       | HA  | 4.47 | 16.8$^a$ | H-5 7.55-7-57 | H-9 7.92 |
|          | HB  | 3.86 | 16.8$^a$ | H-6,7 7.40-7.42 | H-11 7.76 7.7$^b$ |
|          |     |      |           |               | +12.0          |
| 3h       | HA  | 4.49 | 16.9$^a$ | H-5 7.57-7-60 | H-11 8.03 7.5$^b$ |
|          | HB  | 3.96 | 16.9$^a$ | H-6,7 7.40-7.47 | H-12 7.73 7.5$^b$ |
|          |     |      |           |               | +11.4          |
| 3i       | HA  | 4.44 | 16.9$^a$ | H-5 7.55-7-57 | H-9,13 7.58-7.61 |
|          | HB  | 3.92 | 16.9$^a$ | H-6,7 7.40-7.42 | H-11,12 7.42-7.48 |
|          |     |      |           |               | +12.1          |

\textsuperscript{a}J. \textsuperscript{b}J. \textsuperscript{c}J_{\text{H-F}}.
Thus, a plot of $\delta^{(11B)}$ for 3a, 3d-3i compounds versus $\sigma_{\text{Hammett}}$ values (Fig. 2) gives the equation $\sigma_{\text{Hammett}} = -0.666[\delta^{(11B)}] + 7.6224$, with a correlation coefficient $R^2 = 0.9036$. These data confirm that the strength of the N→B coordination bond is governed by electronic factors. The $^{19}$F NMR spectra of 3d and 3g compounds exhibit a triplet of triplets at -113.10 ppm ($J = 9.0, 6.4$ Hz) and a single signal at -61.23 ppm, respectively.

**Figure 1.** Plot of $\delta^{(11B)}$ of compounds 3a, 3d-3i versus $\sigma_{\text{Hammett}}$ values.

The $^{13}$C NMR data for compounds 3a-3i are summarized in Table 2. For all compounds the assignment of C-2 and C-3 are based on HETCOR experiments. Thus C-2 correlates with the signals showing an AB coupling, which appear in the range between 3.86 and 4.49 ppm and C-3 correlates with the single signal between 3.75 and 3.87 ppm. The C-8 signal is not observed in any of the compounds; C9 to C-13 in 3d exhibit a doublet, while C9, C10, C11 and C14 in 3g appear quartets due to coupling with F atoms.

**Mass spectrometry**

The 70 eV EI mass spectra of compounds 3b and 3d-3i do not exhibit the molecular ion, while the spectra of 3a and 3c show the molecular ion. The following important fragment ions are observed, in the spectra of 3a, 3b, as well as 3d-3i; the base peak is at m/z = 91 and corresponds to tropylium ion; 3c exhibits the corresponding base peak at m/z = 198 $[C_6H_5CH_2-C_6H_4OCH_3]^+$. All compounds exhibit the fragment ion $[C_6H_5CH_2-C_6H_2R]^+$ and the fragment ion at m/z = 42 $[CH_2NCH_2]^+$. Compounds 3e, 3i and 3f exhibit fragment ions containing $^{35}$Cl, $^{37}$Cl and $^{79}$Br, $^{81}$Br, respectively. Scheme 2 shows some fragment ions and a possible fragmentation pattern.
Infrared spectroscopy
The IR spectra exhibit the ν(C=O) carbonyl oxygen band in the range between 1758 and 1772 cm\(^{-1}\), and a band due to B-O between 1292 and 1304 cm\(^{-1}\). Also the band due to N→B is in the range between 1026 and 1034 cm\(^{-1}\).

Table 2. \(^{13}\)C NMR data of 3a-3i: δ\(_{C}\) [ppm]

|     | 3a\(^a\) | 3b\(^b\) | 3c\(^c\) | 3d\(^d\) | 3e\(^e\) | 3f\(^f\) | 3g\(^g\) | 3h\(^h\) | 3i\(^i\) |
|-----|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| C-1 | 169.21   | 168.96   | 169.22   | 169.10   | 169.02   | 169.03   | 169.52   | 169.47   | 169.08   |
| C-2 | 57.88    | 58.12    | 57.88    | 57.97    | 57.99    | 58.00    | 58.70    | 58.74    | 58.12    |
| C-3 | 60.83    | 60.86    | 60.88    | 60.79    | 60.80    | 60.83    | 61.30    | 61.37    | 60.84    |
| C-4 | 130.72   | 130.49   | 130.75   | 130.69   | 130.60   | 130.63   | 131.07   | 131.07   | 130.65   |
| C-5 | 131.64   | 131.58   | 131.63   | 131.64   | 131.61   | 131.63   | 132.11   | 132.09   | 131.68   |
| C-6 | 128.92   | 128.88   | 128.93   | 128.93   | 128.89   | 128.92   | 129.38   | 129.38   | 128.96   |
| C-7 | 129.60   | 129.62   | 129.62   | 129.63   | 129.60   | 129.62   | 130.13   | 130.13   | 129.79   |
| C-9 | 132.82   | 133.59   | 134.33   | 135.19   | 134.81   | 135.14   | 129.76   | 127.96   | 132.63   |
| C-10| 128.43   | 128.52   | 113.40   | 114.61   | 19.8\(^f\) | 127.70   | 130.63   | 128.68   | 147.99   | 132.95   |
| C-11| 138.25   | 136.59   | 160.13   | 163.13   | 244.90\(^f\) | 134.12   | 123.06   | 126.25   | 124.48   | 129.01   |
| C-12| 128.43   | 128.52   | 113.40   | 114.61   |        | 127.70   | 130.63   | 129.03   | 129.72   | 129.78   |
| C-13| 132.82   | 133.59   | 134.33   | 135.19   | 134.81   | 135.14   | 137.60   | 140.21   | 131.55   |

\(^a\)CH\(_3\) δ = 21.08. \(^b\)COH δ = 193.42. \(^c\)OCH\(_3\) δ = 54.92. \(^d\)CF\(_3\) δ = 129.56, \(J\(_{CF}\) = 273.30. \(^e\)\(^2\)J\(_{CF}\).\(^f\)\(^3\)J\(_{CF}\).\(^g\)Select bond lengths are: B\(_1\)-O\(_{10}\) 1.466(3), B\(_1\)-O\(_{13}\) 1.472(3), C\(_9\)-O\(_{10}\) 1.320(3), C\(_{12}\)-O\(_{13}\) 1.320(3), C\(_8\)-C\(_9\) 1.502(3), C\(_{11}\)-C\(_{12}\) 1.504(3), C\(_8\)-N\(_1\) 1.495(2), C\(_{11}\)-N\(_1\) 1.489(2). The conformations of the two five-membered rings are different.

X-Ray diffraction
Suitable crystals of 3e for X-ray analysis were obtained from methylene chloride; the molecular structure and crystallographic numbering is showing in figure 2. In general the bond distances are within the values characteristic of analogous compounds. Select bond distances are: B\(_1\)-O\(_{10}\) 1.466(3), B\(_1\)-O\(_{13}\) 1.472(3), C\(_9\)-O\(_{10}\) 1.320(3), C\(_{12}\)-O\(_{13}\) 1.320(3), C\(_8\)-C\(_9\) 1.502(3), C\(_{11}\)-C\(_{12}\) 1.504(3), C\(_8\)-N\(_1\) 1.495(2), C\(_{11}\)-N\(_1\) 1.489(2). The conformations of the two five-membered rings are different.
and they are not planar as indicate by the torsion angles (Table 3). The aryl-B and N-Bn groups are bent away from N-B, as indicated by the angle values C7-N1-B1 112.48° (13) and C14-B1-N1 114.78° (14). The molecular structure establishes the bicyclic structure showing a N→B bond length of 1.683(2) Å, the value being comparable to the N→B bond length in analogous compounds.13,18 This molecule shows a bicyclooctane structure with torsion angle of the junction, 17.25° (20).

Scheme 2. Mass spectral data for compounds 3a-3i.
The molecule in the crystal structure shows the following intramolecular contacts: N₁⋯H₇ₐ 2.0047(218), N₁⋯H₇ₖ 1.9786(198), N₁⋯H₈ₐ 2.0528(265), N₁⋯H₈ₖ 2.0181(307) Å, and O₁₃⋯H₁₉, which are significantly shorter than the sum of the van der Walls radii for nitrogen and hydrogen atoms (2.75Å), as well as oxygen and hydrogen (2.70Å). In addition, the following intermolecular contact is observed between O₁⋯H₁₁ₐ 2.3919(0.0249) Å.

**Table 3.** Selected torsion angles (°) for compound 3e

| Bond                        | Angle (°) ± Error       |
|-----------------------------|-------------------------|
| O₁₀-B₁-N₁-C₈               | 14.19 (0.17)            |
| N₁-B₁-O₁₀-C₉               | 17.11 (0.19)            |
| C₈-C₉-O₁₀-B₁               | 13.38 (0.23)            |
| N₁-C₈-C₉-O₁₀              | 2.30 (0.22)             |
| C₉-C₈-N₁-B₁               | 7.70 (0.18)             |
| O₁₃-B₁-N₁-C₁₁             | 17.93 (0.17)            |
| N₁-B₁-O₁₃-C₁₂             | 11.91 (0.20)            |
| C₁₁-C₁₂-O₁₃-B₁            | 1.0 (0.23)              |
| N₁-C₁₁-C₁₂-O₁₃           | 12.19 (0.22)            |
| C₁₂-C₁₁-N₁-B₁            | 18.02 (0.18)            |

**Figure 2.** Molecular structure of compound 3e.

**Conclusions**

The new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O’,N]boranes 3a-3i were characterized by spectroscopic methods. These compounds exhibit a bicyclic structure due to the presence of an intramolecular N→B coordination bond and it is confirmed by a single crystal x-ray diffraction study of (N→B) 4-chlorophenyl[N-benzyliminodiacetate-O,O’,N]borane 3e. The correlation between δ (¹¹B) of compounds 3a, 3d-3i and σ_Hammett values shows that the strength of the N→B bond depends on the electronic factors of the substituent on the B-phenyl group.
Experimental Section

General Procedures. *N*-benzyliminodiacetic acid 1 was prepared according to our methodology.\(^{24}\) Reagents 2a-2i were purchased from Aldrich Co. \(^{1}H, {^{13}}C\) and \(^{11}B\) NMR spectra were recorded on Jeol GLX-270, Jeol Eclipse-400 and Bruker Avance 300-DPX spectrometers, DMSO-d\(_6\) was used as solvent. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer. Melting points were measured in an open capillary tube on a Gallemkamp MFB-595 apparatus and are uncorrected. The single-crystal X-ray study was performed on an Enraf Nonius Kappa CCD diffractometer. Compound 3e, \(C_{17}H_{15}BClO_4N\) (MW = 343.56), crystallized in the space group P 2\(_1\) 2\(_1\) 2\(_1\), orthorhombic from methylene chloride as colorless flakes, size: 0.12 x 0.1 x 0.9 mm\(^3\) with a = 9.9928(2), b = 11.1546(3), c = 14.5858(3) Å, \(V = 1625.82(6)\) Å\(^3\), \(\alpha = 90.00°, \beta = 90.00°, \gamma = 90.00°, \rho = 1.404\) g/cm\(^3\), \(Z = 4, \mu = 0.256\) mm\(^{-1}\), \(F(000) = 712\). Data collection: a total of 3715 reflections were measured (2° > \(\theta\) > 26°), 3619 were independent and of these 2951 were considered observed \([F_o>4.0\sigma(F_o)]\). Solution and refinement: direct methods, all non hydrogen atoms were refined anisotropically, \(R = 0.0382, Rw = 0.0847, w = 1/\sigma^2,\) GOF = 1.019, largest residual electron density peak/hole in the final difference map: 0.137/-0.211 eÅ\(^{-3}\). Atomic scattering factors were taken from the International Tables for X-ray Crystallography.\(^{25}\) Data reduction were performed by Denzo.\(^{26}\) All calculations were carried out using the SHELXL-97 (Sheldrick 1997)\(^{27}\) and the molecular graphics by Diamond 2.1.\(^{28}\)

The procedure outline is general for the preparation of compounds 3a to 3i

\((N\rightarrow B)\) 4-Methylphenyl[\(N\)-benzyliminodiacetate-\(O,O',N]\]borane (3a). A suspension of 0.40 g (1.79 mmol) of N-benzyliminodiacetic acid 1, 0.24 g (1.79 mmol) of 4-methylphenylboronic acid 2a and 66 ml of a mixture of dimethylsulfoxide/benzene (1/10) was placed into a 100 ml flask equipped with a stirrer and a Dean Stark Trap. The mixture was kept under reflux for 12 h. After being cooled to room temperature, the solvent was evaporated under vacuum. The residue was dissolved in acetone and precipitated with hexane to yield 0.57 g (98%) of compound 3a as a white solid, mp 223-225°C. IR: 3014, 2952, 2866, 1766, 1612, 1538, 1498, 1296, 1240, 1034 cm\(^{-1}\) (KBr). MS: m/z (%), 323 (1), 295 (1), 266 (1), 204 (22), 182 (22), 175 (15), 91 (100), 42 (95). Anal. Calcd. for C\(_{18}\)H\(_{18}\)BNO\(_4\) (323): C, 66.87; H, 5.57; N, 4.33. Found: C, 66.94; H, 5.78; N, 4.23.

\((N\rightarrow B)\) 4-Formylphenyl[\(N\)-benzyliminodiacetate-\(O,O',N]\]borane (3b). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.27 g (1.79 mmol) of 4-formylphenylboronic acid 2b, 0.58 g (95%) of compound 3b were obtained as a white solid, mp 213-215°C. IR: 3008, 2952, 2866, 1766, 1612, 1538, 1498, 1296, 1240, 1088, 1034 cm\(^{-1}\) (KBr). MS: m/z (%), 339 (40), 309 (1), 280 (7), 218 (5), 196 (23), 189 (3), 91 (100), 42 (67). Anal. Calcd. for C\(_{18}\)H\(_{16}\)BNO\(_5\) (337): C, 66.87; H, 5.57; N, 4.33. Found: C, 63.87; H, 5.10; N, 4.10.

\((N\rightarrow B)\) 4-Methoxyphenyl[\(N\)-benzyliminodiacetate-\(O,O',N]\]borane (3c). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.27 g (1.79 mmol) of 4-methoxyphenylboronic acid 2c, 0.59 g (96%) of compound 3c were obtained as a white solid, mp 251-253°C. IR: 3006, 2958, 2840,
1772, 1604, 1570, 1512, 1294, 1246, 1026 cm^{-1} (KBr). MS: m/z (%), 311 (1), 282 (11), 220 (11), 198 (100) 191 (11), 91 (64), 42 (67). Anal. Calcd. for C_{18}H_{18}BNO_{5} (339): C, 63.71; H, 5.30; N, 4.12. Found: C, 63.45; H, 5.25; N, 4.29.

(N→B) 4-Fluorophenyl[N-benzyliminodiacetate-O,O',N]borane (3d). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.25 g (1.79 mmol) of 4-fluorophenylboronic acid 2d, 0.57 g (97%) of compound 3d were obtained as a white solid, mp 227-228°C. IR: 3066, 3010, 2954, 2868, 1772, 1638, 1600, 1508, 1292, 1218, 1036 cm^{-1} (KBr). MS: m/z (%), 311 (1), 282 (11), 220 (11), 198 (100) 191 (11), 91 (64), 42 (67). Anal. Calcd. for C_{18}H_{18}BNO_{5} (339): C, 63.71; H, 5.30; N, 4.12. Found: C, 63.45; H, 5.25; N, 4.29.

(N→B) 4-Chlorophenyl[N-benzyliminodiacetate-O,O',N]borane (3e). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.28 g (1.79 mmol) of 4-chlorophenylboronic acid 2e, 0.58 g (94%) of compound 3e were obtained as a white solid, mp 226-228°C. IR: 3010, 2960, 2866, 1764, 1636, 1590, 1560, 1490, 1224, 1034 cm^{-1} (KBr). MS: m/z (%), 299 (1), 270 (9), 208 (6), 186 (52), 179 (4), 91 (100), 42 (90). Anal. Calcd. for C_{17}H_{15}BFNO_{4} (327): C, 62.38; H, 4.58; N, 4.28. Found: C, 62.34; H, 4.72; N, 4.32.

(N→B) 4-Bromophenyl[N-benzyliminodiacetate-O,O',N]borane (3f). Prepared from 0.40g (1.79 mmol) of compound 1 and 0.36 g (1.79 mmol) of 4-bromophenylboronic acid 2f, 0.64 g (92%) of compound 3f were obtained as a white solid, mp 231-233°C. IR: 3010, 2934, 2860, 1764, 1638, 1584, 1558, 1490, 1240, 1224, 1034 cm^{-1} (KBr). MS: m/z (%), 315 (2), 308 (6), 307 (18), 270 (4), 229 (10), 228 (11), 204 (38), 202 (52), 197 (6), 195 (8), 91 (100), 42 (82). Anal. Calcd. for C_{17}H_{15}BClNO_{4} (343): C, 59.47; H, 4.37; N, 4.08. Found: C, 59.76; H, 4.76; N, 4.06.

(N→B) 3(Trifluoromethyl)phenyl[N-benzyliminodiacetate-O,O',N]borane (3g). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.34 g (1.79 mmol) of 3(trifluoromethyl)phenylboronic acid 2g, 0.63 g (93%) of compound 3g were obtained as a white solid, mp 275-277°C. IR: 3060, 3012, 2938, 2862, 1766, 1638, 1584, 1558, 1490, 1294, 1240, 1224, 1034 cm^{-1} (KBr). MS: m/z (%), 349 (3), 332 (7), 330 (7), 270 (5), 268 (5), 248 (19), 246 (19), 241 (3), 239 (3), 91 (100), 42 (65). Anal. Calcd. for C_{18}H_{15}BF_{3}NO_{4} (377): C, 57.29; H, 3.97; N, 3.71. Found: C, 57.30; H, 3.86; N, 3.86.

(N→B) 3-Nitrophenyl[N-benzyliminodiacetate-O,O',N]borane (3h). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.30 g (1.79 mmol) of 3-nitrophenylboronic acid 2h, it was obtained a white solid, which was washed with chloroform and dissolved with acetone. The mixture was filtered and the solvent was evaporated under vacuum to give 0.32g (50%) of compound 3h, as a white solid product, mp 309-311°C. IR: 3060, 3012, 2938, 2862, 1766, 1612, 1570, 1524, 1304, 1220, 1032 cm^{-1} (KBr). MS: m/z (%), 326 (12), 297 (6), 213 (21), 206 (3), 91 (100), 42 (49). Anal. Calcd. for C_{17}H_{15}BN_{2}O_{6} (354): C, 57.62; H, 4.10; N, 7.90. Found: C, 58.02; H, 4.36; N, 7.57.

(N→B) 3-Chlorophenyl[N-benzyliminodiacetate-O,O',N]borane (3i). Prepared from 0.40 g (1.79 mmol) of compound 1 and 0.30 g (1.79 mmol) of 3-chlorophenylboronic acid 2i, 0.59 g (95%) of compound 3i were obtained as a white solid product, mp 263-265°C. IR: 3066, 3012, 2956, 2862, 1758, 1612, 1570, 1524, 1288, 1230, 1030 cm^{-1} (KBr). MS: m/z (%), 288 (2), 286...
(5), 226 (2), 224 (5), 204 (15), 202 (18), 197 (2), 195 (3), 91 (100), 42 (83). Anal. Calcd. for C\textsubscript{17}H\textsubscript{15}BClNO\textsubscript{4} (343): C, 59.47; H, 4.37; N, 4.08. Found: C, 59.61; H, 4.76; N, 4.06.

**Supplementary Material**

Crystallographic data for 3e has been deposited at the Cambridge Crystallographic Data Center, UK, CCDC as supplementary material No. 275644.

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**References**

1. Baum, G. *J. Organomet. Chem.* 1970, 22, 269.
2. Tung, S. H.; Chang, K. M.; Tah, S. L.; Liu C. C.; Chang, S. L. *Chem. Abstr.* 1967, 66, 37990m.
3. Csuk, R.; Höning, H.; Weidmann, H.; Zimmerman, H. K. *Arch. Pharm.* 1984, 317, 336.
4. Miller III, M. C.; Sood, A.; Spielvogel, B. F.; Hall I. H. *Anticancer Research.* 1997, 17, 3299.
5. Karthikeyan, S.; Sood, A.; Tomas, J.; Spielvogel, B. F.; Hall, I. H. *Amino Acids* 1995, 8, 323.
6. Perks, C. A.; Mill, A. J.; Constantine, G.; Harrison, K. G.; Gibson, J. A. *British J. Radiol.* 1988, 61, 1115.
7. Nemoto, H.; Cai, J.; Asao, N. *J. Med. Chem.* 1995, 38, 1673.
8. Pignol, J. P.; Abbe, J. C.; Lefebvre, O.; Stampfler, A.; Methlin, G.; Sahel, J. C. R. *Acad. Sci. III.* 1994, 317, 543.
9. Mancilla, T.; Contreras, R.; Wrackmeyer, B. *J. Organomet. Chem.* 1986, 307, 1.
10. Mancilla, T.; Gálvez, S. L. *Main Group Met. Chem.* 1992, 15, 9.
11. Mancilla, T.; Alarcón, M. L.; Carrillo, L. *Heteroatom Chem.* 1994, 5, 455.
12. Mancilla, T.; Carrillo, L.; Reduncido, M. P. *Polyhedron.* 1996, 15, 3777.
13. Mancilla, T.; Höpfl, H.; Bravo, G.; Carrillo, L. *Main Group Met. Chem.* 1997, 20, 31.
14. Amaya, D. L.; Calixto, Ma. A. Bachelor thesis, Instituto Tecnológico de Tuxtepec; Cinvestav, 2002. Flores Ancona R. M. Bachelor thesis, Universidad Veracruzana; Cinvestav, 2002.
15. Garrigues. B.; Mullier, M.; Raharinirina, A. *J. Organomet. Chem.* 1986, 302, 153.
16. Mancilla, T.; Contreras, R. *J. Organomet. Chem.* 1987, 321, 191.
17. Contreras, R.; García, C.; Mancilla T.; Wrackmeyer B.; *J. Organomet. Chem.* 1983, 246, 213.
18. Farfán, N.; Mancilla, T.; Castillo, D.; Uribe, G.; Carrillo, L.; Joseph-Nathan, P.; Contreras R. *J. Organomet. Chem.* 1990, 381, 1.
19. Barba, V.; Cuahutle, D.; Ochoa, Ma. E.; Santillan, R.; Farfán, N. *Inor. Chim. Acta* 2000, 303, 7.
20. Farfán, N.; Höpfl, H., Barba, V.; Ochoa, Ma. E.; Santillan, R.; Gómez, E.; Gutiérrez, A. *J. Organomet. Chem.* 1999, 581, 70.
21. Farfán, N.; Santillan, R.; Höpfl, H. *Main Group Chem. News* 1999, 7, 5.
22. Johnson, C. D. The Hammett Equation, Cambridge University Press: 1980, 3, 25.
23. Bondi, A. *J. Phys. Chem.* 1964, 68, 441.
24. Zamudio-Rivera, L. S. Ph.D. thesis, Cinvestav, 2001
25. Cromer, D. T.; Waber, I. T. *International Tables for x-ray Crystallographic Data*, Kynoch Press: England, 1974; Vol. IV.
26. (a) Otwinowski, Z.; Minor, W. In *Processing of x-ray Diffraction Collection in Oscillation Mode*; Carter, C. W.; Sweet, R. M., Eds; Academic Press, 1996. (b) Prince, E. *Methods Enzymol.* 1997, 276, 307.
27. Sheldrick, G. M. *SHELX-97*, Program for Crystal Structure Solution, University of Göttingen, Germany, 1993.
28. Farrugia, L. J. *J. Appl. Crystallogr.* 1999, 32, 837.