Synthesis and Characterization of New Diazenecarboxamide Ligands Using a Selective Adduct Formation with B(C₆F₅)₃

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The synthesis and structure of new N-(2,6-diisopropylphenyl)-2-phenyldiazenecarboxamide (L₁) and N-(2,6-diisopropylphenyl)-2(perfluorophenyl) diazenecarboxamide (L₂) ligands are described. The subsequent reactions of ligands L₁, L₂ and L₃ with trispentafluorophenylboron gave rise to new adducts (A₁), (A₂) and (A₃), where B(C₆F₅)₃ is coordinated to the carbonyl group. New ligands and adducts are characterized by nuclear magnetic resonance (NMR), infrared (IR), and elemental analysis techniques. The crystal structures of all compounds are obtained and described.

Keywords: diazenecarboxamide ligands, borane adduct, azo compounds

Introduction

Azo compounds have caused great interest in organic synthesis,¹,² they have been utilized as dyes and analytical reagents,³ and as a material for nonlinear optics and for optics information storage in laser disks.⁴,⁵ Recently, many studies have shown that some azo compounds possess excellent optical memory and photoelectric properties.⁶,⁷ These types of ligands have been explored also as potential modulators of drug resistance to cisplatin for certain types of tumors,⁸,⁹ but their coordination chemistry has not been explored.

Among the variety of organic compounds that can act as ligands, the diazenecarboximidates seem to be good candidates because of their structural “similarity” with α-iminocarboxamides, especially considering the various modes of coordination that they can present (NN, NO and η¹-NO).

The basis of the development of new catalysts for different processes continues to be centered on the design of organic compounds capable not only to stabilize a metallic center, but also to allow greater control of their reactivity and selectivity in a given catalytic process.¹⁰-¹⁸ An interesting series of catalysts similar to α-diimines¹⁹-²² have been reported recently (Figure 2),²³-²⁹ in which the ligands contain Lewis base groups such as cyano, carbonyl or other heteroatoms in addition to those coordinated with the metallic center, i.e., with exocyclic functionalities.

We have therefore focused on the design of a series of new diazenecarboxamide ligands differing in electronic and steric properties. We have prepared the corresponding adduct with B(C₆F₅)₃ (BCF) to deduce how it interacts with the heteroatoms in the molecule and if the ligand has a preferred site of coordination to a Lewis acid.

![Azo compounds.](image-url)

[Note: The image reference is not provided in the text, and the figure should be included as per the instruction.]
Experimental

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich, unless otherwise specified. Toluene, tetrahydrofuran (THF), ether, and pentane were distilled from benzophenone ketyl. Trispentafluorophenylborane (B(C₆F₅)₃) was sublimed at 65 °C under static vacuum and stored in the glovebox. The following instruments were used for the physical characterization of the compounds. Nuclear magnetic resonance (NMR) spectra were obtained on Bruker DRX 400, AVANCE 400 MHz, and AVANCE III 400 MHz spectrometers. ¹H and ¹³C {¹H} chemical shifts were referenced to residual proton and naturally abundant ¹³C resonances of the deuterated solvent, respectively, relative to tetramethylsilane. Most NMR assignments were supported by additional 2D experiments. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets, and in solution using C₆D₆ as solvent.

Synthesis of N₂-diphenyldiazenecarboxamide (L₁)

Phenyl isocyanate (1.38 g; 11.6 mmol) was added to a solution of phenylhydrazine (1.25 g; 11.6 mmol) in anhydrous acetonitrile (40 mL). The mixture was stirred for 1 h. A white precipitate was formed. The solvent was evaporated under vacuum to obtain (2.39 g; 10.5 mmol) of intermediate product C₆H₅NHNHCONHC₆H₅. The crude product was then suspended in a mixture of CH₂Cl₂/CH₃OH (5:1) and pyridine (0.83 g; 10.5 mmol). The solution was cooled in water, and (1.91 g; 10.7 mmol) N-bromosuccinimide was added dropwise during 5 min with stirring. The solution changed its color to deep red. The resulting solution was stirred for 10 min at room temperature and was washed consecutively with water (2 × 15 mL), 10% NaOH (10 mL), and water (2 × 15 mL). The solution was dried over MgSO₄, filtered and evaporated under vacuum. The crude product was dissolved in minimum amounts of methanol and recrystallized; an orange solid was obtained and washed with cool hexane, yield 2.07 g (79.5%).

IR (KBr) νmax / cm⁻¹: 3261, 3233, 3192, 3134, 3078, 3060, 3020, 1700, 1604, 1555, 1492, 1442, 1319, 1306, 1254, 1180, 1142, 976, 779, 756, 692, 681, 574, 498, 472; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.69 (s, 1H, NH), 7.96 (d, 2H, J 7.1 Hz, Ar-H), 7.75 (d, 2H, J 7.5 Hz, Ar-H), 7.62 (t, 1H, Ar-H), 7.55 (t, 2H, J 7.4 Hz, Ar-H), 7.42 (t, 2H, Ar-H), 7.21 (t, 1H, J 7.4 Hz, Ar-H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.9, 151.6, 137.6, 134.6, 130.0, 129.8, 125.4, 1180, 1142, 976, 779, 756, 692, 681, 574, 498, 472; anal. calcd. for C₁₃H₁₁N₃O: C, 69.32; H, 4.92; N, 18.66; found: C, 69.27; H, 4.56; N, 18.81.

N-(2,6-Diisopropylphenyl)-2-phenyldiazenecarboxamide (L₂)

Using the same procedure as for the synthesis of L₁, (2,6-diisopropylphenyl)isocyanate (0.79 g; 3.91 mmol), phenylhydrazine (0.42 g; 3.91 mmol), C₆H₅NHNHCONH₂,₂,₆-iPr₂C₆H₃ (0.21 g; 2.71 mmol) and N-bromosuccinimide (0.49 g; 2.75 mmol) were used to obtain the orange solid L₂; yield 0.63 g (52%).

IR (KBr) νmax / cm⁻¹: 3231, 3056, 2965, 1702, 1498, 1468, 1451, 1217, 1203, 1183, 1153, 796, 781, 762, 730, 684, 1H NMR (400 MHz, CD₂Cl₂) δ 8.03 (d, 2H, J 7.0 Hz, Ar-H), 7.88 (s, 1H, NH), 7.65 (m, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.40 (t, 1H, J 7.7 Hz, Ar-H), 7.28 (d, 2H, J 7.8 Hz, Ar-H), 3.19 (m, 2H, J 6.9 Hz, CH-iPr), 1.23 (d, 6H, J 6.9 Hz, CH₃); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.9, 151.6, 137.6, 134.6, 130.0, 129.8, 125.4, 124.5, 120.3; anal. calcd. for C₁₉H₂₃N₃O: C, 73.76; H, 7.49; N, 13.58; found: C, 73.47; H, 7.51; N, 13.68.

N-(2,6-Diisopropylphenyl)-2-(perfluorophenyl)diazene-carboxamide (L₃)

Using the same procedure as for the synthesis of L₁, (2,6-diisopropylphenyl)isocyanate (1.50 g; 7.4 mmol), pentafluorophenyl hydrazine (1.4 g; 7.4 mmol), C₆F₅NHNHCONH₂,₂,₆-iPr₂C₆H₃ (2.7 g; 2.75 mmol) were used to obtain the orange solid L₃; yield 0.63 g (52%).

IR (KBr) νmax / cm⁻¹: 3261, 3233, 3192, 3134, 3078, 3060, 3020, 1700, 1604, 1555, 1492, 1442, 1319, 1306, 1254, 1180, 1142, 976, 779, 756, 692, 681, 574, 498, 472; ¹H NMR (400 MHz, CD₂Cl₂) δ 7.88 (s, 1H, NH); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.9, 151.6, 137.6, 134.6, 130.0, 129.8, 125.4, 124.5, 120.3; anal. calcd. for C₁₉H₁₅Ni₃O: C, 69.32; H, 4.92; Ni, 13.58; found: C, 69.27; H, 4.56; Ni, 13.86.
pyridine (0.53 g; 6.7 mmol) and N-bromosuccinimide (1.24 g; 6.9 mmol) were used to obtain the orange solid \( L_1 \); yield 1.49 g (49%).

IR (KBr) \( \nu_{\text{max}} / \text{cm}^{-1} \) 3187, 2969, 1693, 1523, 1515, 1491, 1407, 1313, 1032, 975, 798, 748; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.80 (s, 1H, NH), 7.41 (t, 1H, \( J = 7.7 \text{ Hz, Ar-H} \)), 7.28 (d, 2H, \( J = 7.7 \text{ Hz, Ar-H} \)), 3.16 (m, 2H, \( J = 6.8 \text{ Hz, CH-iPr} \)); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 159.3, 147.0, 130.1, 129.8, 124.4, 29.5, 24.0; anal. calcd. for \( \text{C}_9\text{H}_7\text{F}_2\text{N}_2\text{O} \): C, 47.86; H, 2.00; N, 4.57; found: C, 48.76; H, 1.98; N, 4.67.

N,N-Diphenylidiazene-carboxamide-B(C\(_6\)F\(_3\)) \( (A_1) \)

A solution of B(C\(_6\)F\(_3\)) \((0.11 \text{ g; } 0.13 \text{ mmol})\) in anhydrous dichloromethane was added to \( L_1 \) (0.05 \text{ g; } 0.13 \text{ mmol}) previously dissolved in anhydrous dichloromethane. The mixture was stirred for 2 h at RT. The solution was filtered and evaporated to dryness. The solid was washed twice with anhydrous pentane and dried in vacuum to obtain \( A_1 \) as a red solid in quantitative yield. Single red crystals of \( A_1 \) suitable for X-ray crystal structure analysis were obtained from dichloromethane/pentane by the diffusion method.

IR (KBr) \( \nu_{\text{max}} / \text{cm}^{-1} \) 3337, 3067, 2978, 2958, 2936, 2874, 1649, 1585, 1518, 1454, 1381, 1353, 1316, 1247, 1207, 1152, 978, 766, 674; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.22 (s, 1H, NH), 7.83 (dd, 2H, Ar-H), 7.79 (t, 1H, \( J = 7.7 \text{ Hz, Ar-H} \)), 7.69 (dd, 2H, \( J = 7.7 \text{ Hz, Ar-H} \)), 7.61 (t, 2H, \( J = 7.7 \text{ Hz, Ar-H} \)), 7.53 (t, 2H, \( J = 7.7 \text{ Hz, Ar-H} \)), 7.47 (t, 1H, \( J = 7.7 \text{ Hz, Ar-H} \)); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 160.8, 151.0, 138.9, 132.6, 130.9, 129.8, 126.7, 123.2; \(^{19}\)F NMR (370 MHz, CDCl\(_3\)) \( \delta \) -132.5, -156.2, -163.4; \(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \( \delta \) -3.78 ppm (\( \nu_{1/2} \text{ ca. } 800 \text{ Hz} \)); anal. calcd. for \( \text{C}_{16}\text{H}_{19}\text{BF}_3\text{N}_2\text{O} \): C, 53.80; H, 4.54; N, 10.52; found: C, 57.25; H, 4.08; N, 10.64.

N-(2,6-Diisopropylphenyl)-2-(perfluorophenyl)diazene-carboxamide-B(C\(_6\)F\(_3\)) adduct \( (A_2) \)

This compound was obtained by the same procedure as for the synthesis of \( A_1 \), but with B(C\(_6\)F\(_3\)) \((0.06 \text{ g; } 0.13 \text{ mmol})\) and \( L_2 \) (0.05 \text{ g; } 0.13 \text{ mmol}).

IR (KBr) \( \nu_{\text{max}} / \text{cm}^{-1} \) 3317, 2973, 2935, 1647, 1468, 1397, 1330, 1288, 1259, 1172, 1106, 1035, 980, 801, 678; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.49 (s, 1H, NH), 7.48 (t, 1H, \( J = 7.8 \text{ Hz, Ar-H} \)), 7.29 (d, 2H, \( J = 7.8 \text{ Hz, Ar-H} \)), 2.95 (m, 2H, \( J = 6.8 \text{ Hz, CH-iPr} \)), 1.15 (d, 6H, \( J = 6.8 \text{ Hz, CH}_3 \)); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 163.1, 146.4, 127.1, 131.3, 124.8, 29.4, 23.7; \(^{19}\)F NMR (370 MHz, CDCl\(_3\)) \( \delta \) -123.2, -132.9, -155.8, -156.7, -162.3, -163.1; \(^{11}\)B NMR (160 MHz, CDCl\(_3\)) \( \delta \) -6.02 ppm (\( \nu_{1/2} \text{ ca. } 1100 \text{ Hz} \)); anal. calcd. for \( \text{C}_{17}\text{H}_{15}\text{BF}_3\text{N}_2\text{O} \): C, 48.76; H, 1.99; N, 4.61; found: C, 49.01; H, 2.15; N, 4.67.

X-ray diffraction

Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT; \(^{30}\) data reduction Denzo-SMN; \(^{31}\) absorption correction, Denzo; \(^{32}\) structure solution SHELXS-97; \(^{33}\) structure refinement SHELXL-97; \(^{34}\) and graphics, XP. \(^{35}\) Thermal ellipsoids are shown with 30\% probability. R-values are given for observed reflections, and wR\(^2\) values are given for all reflections.

Exceptions and special features

Comounds \( L_1, L_3, A_1, A_2 \) and \( A_3 \) crystallized with two molecules in the asymmetric unit. In all compounds (\( L_1, L_3, A_1, A_2 \) and \( A_3 \)) the hydrogen atom at nitrogen N1 was refined freely.

**Results and Discussion**

**Synthesis of ligands**

Scheme 1 shows the synthetic pathway to the diazenecarboxamide ligand. \(^{38,39}\) The reaction sequence begins with the addition of the monosubstituted hydrazine derivative to the isocyanate at RT, resulting in the formation of the corresponding 1,4-disubstituted semicarbazide. Oxidation of the semicarbazide with N-bromosuccinimide/pyridine...
(NBS/Py) yields the desired compound. See Experimental and Supplementary Information (SI) sections.

The symmetric (L1) and asymmetric (L2 and L3) diazenecarboxamide ligands were purified by crystallization in methanol, in 80, 52 and 49% yield, respectively. In each case the 1H, 13C NMR spectra (in [D2]-dichloromethane) are consistent with the exclusive formation of one product. In the case of L3, the three signals in the 19F NMR spectrum at -138.8(o), -139.3(p), and -153.9(m) ppm confirm the formation of this compound. For details, see Table 1 and SI section.

FTIR spectroscopy shows bands at 1700, 1702 and 1693 cm-1 for L1, L2 and L3, respectively, due to the C=O functionality.

Solid-state characterization of L1 by single-crystal X-ray diffraction (Figure 3) is consistent with the structure in Scheme 1. Compound L1 adopts a close coplanar geometry [N4−N3−C2−N1, dihedral angle −168.7(1)°] including the two phenyl rings with a trans relation around the N=N double bond between the phenyl and the carboxamide oxygen fragment (Table 2). Angles O1−C2−N1 and O1−C2−N3 are 127.3(1)° and 124.4(1)°, indicating a slight distortion from the ideal planar trigonal geometry, while the N3−N4, N3−C2 and N1−C2 bond distances are 1.246(2), 1.466(2) and 1.338(2)Å, consistent with a double and single bond character, respectively.

Also, single crystals of L2 suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent from a concentrated ether solution at RT. The results of this study are shown in Figure 4. The molecular structure of L2 shows that the N3−N4 bond is slightly out of the C2 sp2 plane (they are not coplanar). However, N3 and N1 are on the same side of the structure. The O1−C2−N3 and O1−C2−N1 angles are not equal, [116.5(2)° and 126.8(2)°], due to increased steric hindrance near the N1 atom. The N3−N4, C2−O1 and N3−C2, N1−C2 bond distances are 1.227(3), 1.217(3) Å, and 1.464(3) and 1.333(3) Å, indicating double and single bond character, respectively. For details see Table 2 and SI section.

Single crystals of L3 suited for X-ray crystal structure analysis were obtained by slow evaporation of an ether solution at RT (Figure 5). This analysis shows that ligand L3.

| Table 1. Selected spectroscopic parameters of the diazenecarboxamide ligands L1, L2, L3, and the diazenecarboxamide-BCF adducts A1, A2, and A3 |
|-----------------------------|----------------|----------------|----------------|----------------|----------------|
|  | L1  | L2  | L3  | A1  | A2  | A3  |
| NMR δH / ppm              |               |               |               |               |               |
| N−H                        | 8.69          | 8.03          | 7.80          | 9.22          | 8.61          | 8.49          |
| HCiPr                      | –             | 3.19          | 3.16          | –             | 2.99          | 2.95          |
| MeiPr                      | –             | 1.23          | 1.24          | –             | 1.18          | 1.15          |
| NMR δC / ppm               |               |               |               |               |               |
| (C=O)                      | 157.9         | 160.4         | 159.3         | 160.8         | 163.8         | 162.9         |
| FTIR / cm⁻¹                |               |               |               |               |               |
| ν(C=O)                     | 1700          | 1702          | 1693          | 1646          | 1649          | 1648          |

Scheme 1. Synthetic pathway to the diazenecarboxamide ligand.
Synthesis and Characterization of New Diazenecarboxamide Ligands


The diazenecarboxamide ligand has a similar topology as \( L_2 \) (Figure 4). This can be seen in the \( \text{N}4\)-\( \text{N}3\)-\( \text{C}2\)-\( \text{N}1 \) dihedral angle (68.9(2)°) compared with \( L_2 \) (31.0(4)°), as well as the angles around \( \text{C}2 \) (\( \text{N}3\)-\( \text{C}2\)-\( \text{O}1 \) and \( \text{N}1\)-\( \text{C}2\)-\( \text{O}1 \), which are 118.0(2)° and 128.0(2)°, respectively.

This can also be observed in the \( \text{N}4\)-\( \text{N}3\), \( \text{C}2\)-\( \text{O}1 \) and \( \text{N}3\)-\( \text{C}2\), \( \text{N}1\)-\( \text{C}2 \) bond lengths, which are 1.233(2), 1.217(2), and 1.462(3), 1.321(3) Å, indicating double and single bond character, respectively, as previously observed in ligand \( L_2 \).

For details, see Table 2 and SI section.

Reaction of the diazenecarboxamide ligand with \( \text{B(C}_{6}\text{F}_{5})_3 \)

We decided to investigate the diazenecarboxamide ligand’s affinity for \( \text{B(C}_{6}\text{F}_{5})_3 \) by stirring of the reaction mixture of the respective ligand \( (L_1-L_3) \) plus one equivalent of \( \text{B(C}_{6}\text{F}_{5})_3 \) for 2 h at RT in dichloromethane (DCM), eventually yielding adduct \( A_1-A_3 \) [i.e., \( L_1\)-\( \text{B(C}_{6}\text{F}_{5})_3 \)] as a red crystalline solid in 100% isolated yield (Scheme 2). Single crystals of \( A_1-A_3 \) suitable for X-ray crystal structure analysis were obtained from DCM/pentane by the diffusion method.

The X-ray crystal structure analysis of compound \( A_1 \) (Figure 6), unlike the free ligand, features a U-shaped NNCN section of the framework (torsion angle \( \text{N}4\)-\( \text{N}3\)-\( \text{C}2\)-\( \text{N}1 \) is -16.8(3)°). The internal bonding situation is found to be asymmetric. The \( \text{N}3\)-\( \text{N}4 \) bond (1.249(2) Å) is markedly shorter than the opposite \( \text{N}3\)-\( \text{C}2 \) and \( \text{N}1\)-\( \text{C}2 \) bonds, 1.423(3) and 1.308(3) Å, and consequently the \( \text{C}2\)-\( \text{O}1 \) bond (1.260(3) Å) is shorter and consistent with a double bond character.

Carbon atom \( \text{C}2 \) is trigonal planar (sum of the bond angles at \( \text{C}2 \) 360.0°). The \( \text{B(C}_{6}\text{F}_{5})_3 \) Lewis acid is found to be coordinated with the oxygen atom (Figure 6). The boron atom shows a distorted tetrahedral coordination geometry with typical bond angles of 109.3(2)° (\( \text{O}1\)-\( \text{B}1\)-\( \text{C}31 \)), 101.1(2)° (\( \text{O}1\)-\( \text{B}1\)-\( \text{C}41 \)), and 108.8(2)° (\( \text{O}1\)-\( \text{B}1\)-\( \text{C}51 \)). The \( \text{C}2\)-\( \text{O}1\)-\( \text{B}1 \) unit has a bent molecular geometry (angles \( \text{C}2\)-\( \text{O}1\)-\( \text{B}1 \) 131.5(2)°). The \( \text{O}1\)-\( \text{B}1 \) bond length (1.565(3) Å) is within the typical O–B single bond range. The \( \text{C}2\)-\( \text{O}1 \) bond length is 0.043 Å longer than the distance in \( L_1 \) after coordination with BCF.

The IR spectrum of the \( A_1 \) borane adduct shows a strong \( \text{C}=\text{O} \) stretching band at \( \tilde{v}= 1646 \text{ cm}^{-1} \), which is shifted by \( \tilde{v}= 54 \text{ cm}^{-1} \) to lower wavenumber compared to its parent \( L_1 \).

### Table 2. Selected bond lengths (Å) and angles (degree) for compounds \( L_1, L_2, L_3, A_1, A_2 \) and \( A_3 \)

<table>
<thead>
<tr>
<th></th>
<th>( L_1 )</th>
<th>( L_2 )</th>
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<th>( A_1 )</th>
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<td>( \text{O}(1))-( \text{C}(2) )</td>
<td>1.217(2)</td>
<td>1.217(3)</td>
<td>1.217(2)</td>
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<td>1.262(2)</td>
<td>1.251(4)</td>
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<td>1.333(3)</td>
<td>1.321(3)</td>
<td>1.308(3)</td>
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<tr>
<td>( \text{N}(3))-( \text{C}(2) )</td>
<td>1.466(2)</td>
<td>1.464(3)</td>
<td>1.462(3)</td>
<td>1.423(3)</td>
<td>1.432(3)</td>
<td>1.434(5)</td>
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<tr>
<td>( \text{N}(3))-( \text{N}(4) )</td>
<td>1.246(2)</td>
<td>1.227(3)</td>
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<td>( \text{O}(1))-( \text{B}(1) )</td>
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<td>Bond Angles (°)</td>
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<tr>
<td>( \text{O}(1))-( \text{C}(2))-( \text{N}(1) )</td>
<td>127.3(1)</td>
<td>126.8(2)</td>
<td>128.0(2)</td>
<td>121.7(2)</td>
<td>121.1(2)</td>
<td>121.3(3)</td>
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<td>( \text{O}(1))-( \text{C}(2))-( \text{N}(3) )</td>
<td>124.4(1)</td>
<td>116.5(2)</td>
<td>118.0(2)</td>
<td>118.5(2)</td>
<td>118.8(2)</td>
<td>118.1(3)</td>
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<tr>
<td>( \text{O}(1))-( \text{B}(1))-( \text{C}(41) )</td>
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<td>111.0(2)</td>
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<tr>
<td>( \text{O}(1))-( \text{B}(1))-( \text{C}(51) )</td>
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<td>-</td>
<td>108.8(2)</td>
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<td>104.5(3)</td>
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<td>( \text{O}(1))-( \text{B}(1))-( \text{C}(61) )</td>
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<td>( \text{O}(1))-( \text{B}(1))-( \text{C}(31) )</td>
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<td>109.3(2)</td>
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</table>

Figure 4. Molecular structure of the \( L_2 \) ligand (thermal ellipsoids are shown at 30% probability).

Figure 5. Molecular structure of the \( L_1 \) ligand. Only one of the two independent molecules found in the asymmetric unit is shown (thermal ellipsoids are shown at 30% probability).
ligand. This is what would be expected from simple addition of a carbonyl to a strong Lewis acid: sharing of the oxygen lone pair with the boron atom effectively reduces overlap, making the double bond slightly weaker, consistent with what we found by the X-ray crystal analysis made above.

In the $^1$H NMR spectrum of $A_1$, the N–H resonance at $\delta$ 9.22 ppm (in [D$_2$]-dichloromethane) is observed. The $^{11}$B NMR spectrum features a typical four-coordinate boron resonance ($\delta$ -3.78 ppm), which is supported by a characteristically small $\Delta\delta$ (p,m) C$_6$F$_5$ chemical shift difference$^{41-44}$ in the $^{19}$F NMR spectrum [$\delta$ −132.5 (o), −156.2 (p), −163.4 (m)]. Adduct $A_1$ shows a characteristic $^{13}$C resonance for the C=O--B units ($\delta$ $^{13}$C: 168.8 ppm).

Treatment of $L_2$ with one molar equivalent of B(C$_6$F$_5$)$_3$ in DCM at RT (2 h) led to complete conversion to $A_2$, which was isolated from the reaction mixture in quantitative yield. Single crystals of $A_2$ were obtained at RT from DCM/pentane by the diffusion method.

The X-ray crystal structure analysis of compound $A_2$ confirms the formation of a Lewis acid/Lewis base adduct, by coordination of BCF with the carbonyl functionality (Figure 7). As expected, the U configuration of the parent ligand $L_2$ is found to be nearly unperturbed upon adduct formation with B(C$_6$F$_5$)$_3$, as seen in $A_1$.

The boron atom has taken a distorted tetrahedral coordination geometry in the adduct. It features bond angles of 111.0(2)$^\circ$ (O1–B1–C41), 106.0(2)$^\circ$ (O1–B1–C51), and 102.1(2)$^\circ$ (O1–B1–C61). The B1–O1 bond length is 1.577(3) Å. The C2–O1 double bond (1.262(2) Å) is 0.043 Å longer than the C2–O1 bond in $L_2$ (a similar variation was observed in $A_1$). The central carbon atom C2 of the framework is trigonal planar (sum of the bond angles 359.8°). The central N=N double bond unit has a bond length of 1.252(2) Å, while the bond lengths of N3–C2 and C2–N1 are 1.432(3) and 1.309(3) Å, respectively. There is bond length alternation toward the carbonyl. An effect is also seen on the C2–N1 bond length, which is 0.024 Å smaller compared to that of the free ligand (Figure 4 and Table 2). Similarly to $A_1$, the IR spectrum of the borane adduct $A_2$ shows a strong C=O stretching band at $\tilde{\nu}$ = 1648 cm$^{-1}$, which is shifted by $\tilde{\nu}$ = 53 cm$^{-1}$ to lower wavenumbers compared to its parent ligand $L_2$, Table 1, consistent with the weakness of the carbonyl bond, which is seen from the X-ray crystal analysis mentioned above (Table 2).

In the NMR spectrum of $A_2$, the typical signals for the amide unit [$^1$H: $\delta$ 8.61 –NH; $^{13}$C: $\delta$ 164.2, (C=O–)] are observed. The $^{11}$B NMR spectrum features a typical four-coordinate boron resonance ($\delta$ −4.41 ppm), and the
$^{19}$F NMR signals at $\delta -132.5$ ($\alpha$), $-157.0$ ($p$), and $-164.0$ ($m$) for the C$_g$F$_3$ substituents on boron.

Finally, the addition of one molar equivalent of B(C$_g$F$_3$)$_3$ to L$_1$ in DCM at RT (2 h) also led to complete conversion to A$_1$, which was isolated from the reaction mixture in quantitative yield. Single crystals of A$_3$ were obtained in the same way as for A$_1$ and A$_2$.

As expected, the crystal structure analysis (Figure 8) shows that the carbonyl functionality of L$_1$ is coordinated by B(C$_g$F$_3$)$_3$. (O1–B1 1.593(5) Å, angles O1–B1–C41 109.0(3)$^\circ$, O1–B1–C51 105.5(3)$^\circ$, O1–B1–C61 101.9(3)$^\circ$). The bond length differences in the internal fragment’s diazene double bond, N3–N4 1.242(4) Å, N3–C2 1.434(5) Å and N1–C2 1.306(5) Å, are in the range of those for the other adducts (A$_1$ and A$_2$).

In solution, compound A$_3$ has a $^{13}$C NMR signal for the carbonyl carbon atom (C2) at $\delta$ 162.8 ppm. As expected, a single set of C$_g$F$_3$ resonances at $\delta$ $-132.9$ ($\alpha$), $-156.7$ ($p$), and $-163.1$ ppm ($m$) was observed for the B(C$_g$F$_3$)$_3$ group coordinated with the carbonyl function (Scheme 2), and the corresponding $^{11}$B NMR resonance was found at $-6.02$. The C$_g$F$_3$ ring produced a single set of $\alpha$, $p$- and $m$- $^{19}$F NMR resonances at $\delta$ $-132.2$, $-155.8$, and $-162.3$ ppm, respectively.

Conclusions

As stated in the introduction, our interest in this study was the synthesis and characterization of a variety of new ligands with additional functionality in the framework, which would allow the coordination to the metal center and to the other atoms. This means that there will be a free functional group, with lone electron pairs after the formation of the complexes. Scheme 1 provides a straightforward approach to generate diazenecarboxamide ligands in which the steric bulk on the diazene and carboxamide nitrogens can be controlled by aromatic substituents. Furthermore, the diazenecarboxamide-B(C$_g$F$_3$)$_3$ adduct has been isolated and fully characterized. The binding of B(C$_g$F$_3$)$_3$ with the carbonyl functionality (Scheme 2) results in a unique adduct formation. This species has more acidic NH protons, as was shown by the shift of the resonance (more than 0.53 ppm) toward low field compared to the free ligand. This is due to a redistribution of electron density within the electronically delocalized ligand-BCF framework.

Supplementary Information

Supplementary data (further experimental and spectroscopic details, CCDC reference numbers 1005207-1005212 and potential energy profiles for the deprotonated form of ligands L$_2$ and L$_3$) are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

The authors acknowledge the financial support by CONICYT through FONDECYT projects 1100286, 1130077 and Milenium Nucleus NC120082. M. E. acknowledges funding through a CONICYT PhD fellowship.

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Submitted: April 13, 2015
Published online: October 21, 2015