Article

Synthesis and Characterization of New Diazenecarboxamide Ligands Using a Selective Adduct Formation with B(C$_6$F$_5$)$_3$

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The synthesis and structure of new *N*-(2,6-diisopropylphenyl)-2-phenyldiazenecarboxamide (L$_2$) and *N*-(2,6-diisopropylphenyl)-2 (perfluorophenyl) diazenecarboxamide (L$_3$) ligands are described. The subsequent reactions of ligands L$_1$, L$_2$ and L$_3$ with trispentafluorophenylboron gave rise to new adducts (A$_1$), (A$_2$) and (A$_3$), where B(C$_6$F$_5$)$_3$ 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 non linear 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 diazenecarboximides 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 η^3-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-diimines[19-22] 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(C$_6$F$_5$)$_3$ (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.
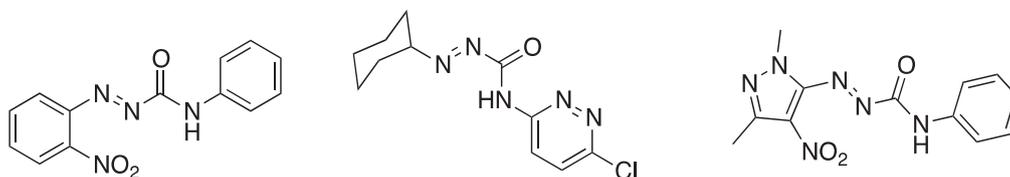
Figure 1. Azo compounds.

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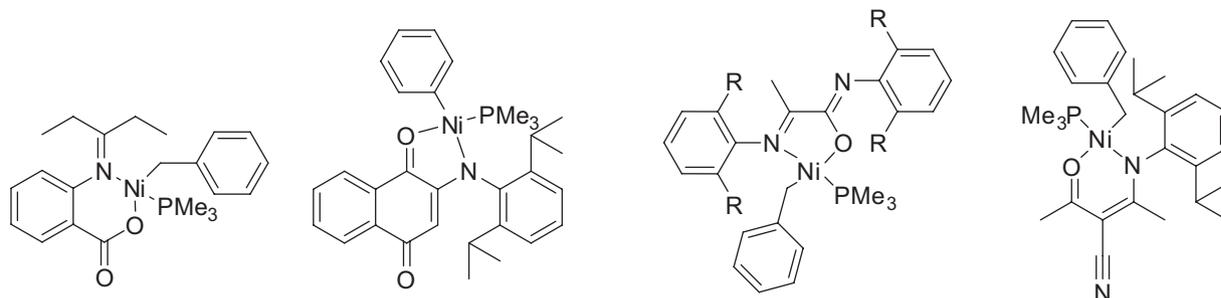
Figure 2. Examples of complexes with basic exocyclic functionalities.

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 ($B(C_6F_5)_3$) 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. Nucelar magnetic resonance (NMR) spectra were obtained on Bruker DRX 400, AVANCE 400 MHz, and AVANCE III 400 MHz spectrometers. ^1H and ^{13}C {^1H} chemical shifts were referenced to residual proton and naturally abundant ^{13}C 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 C_6D_6 as solvent.

Synthesis of *N*,2-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 $C_6H_5NHNHCONHC_6H_5$. The crude product was then suspended in a mixture of CH_2Cl_2/CH_3CH_2OH (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) v_{max} / 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, CD_2Cl_2) 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); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 157.9, 151.6, 137.6, 134.6, 130.0, 129.8, 125.6, 124.5, 120.3; anal. calcd. for $C_{13}H_{11}N_3O$: 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), $C_6H_5NHNHCONH$ 2,6-iPr₂C₆H₃ (0.84 g; 2.71 mmol), pyridine (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) v_{max} / cm⁻¹ 3231, 3056, 2965, 1702, 1498, 1468, 1451, 1217, 1203, 1183, 1153, 796, 781, 762, 730, 684; ^1H NMR (400 MHz, CD_2Cl_2) 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); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.4, 151.7, 147.2, 134.5, 130.8, 130.0, 129.4, 124.6, 124.3, 29.4, 24.0; anal. calcd. for $C_{19}H_{23}N_3O$: 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), $C_6F_5NHNHCONH$ 2,6-iPr₂C₆H₃ (2.7 g; 6.7 mmol),

pyridine (0.53 g; 6.7 mmol) and *N*-bromosuccinimide (1.24 g; 6.9 mmol) were used to obtain the orange solid L_3; yield 1.43 g (49%).

IR (KBr) ν_{max} / cm^{-1} 3187, 2969, 1693, 1523, 1515, 1491, 1407, 1313, 1135, 1032, 975, 798, 748; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.80 (s, 1H, NH), 7.41 (t, 1H, *J* 7.7 Hz, Ar-H), 7.28 (d, 2H, *J* 7.7 Hz, Ar-H), 3.16 (m, 2H, *J* 6.8 Hz, CH-iPr), 1.24 (d, 6H, *J* 6.8 Hz, CH$_3$-iPr); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 159.3, 147.0, 130.1, 129.8, 124.4, 29.5, 24.0; anal. calcd. for C$_{19}$H$_{18}$F$_5$N$_3$O: C, 57.14; H, 4.54; N, 10.52; found: C, 57.25; H, 4.08; N, 10.64.

N,2-Diphenyldiazenecarboxamide-B(C$_6$F$_5$)$_3$ (A$_1$)

A solution of B(C$_6$F$_5$)$_3$ (0.11 g; 0.13 mmol)) in anhydrous dichloromethane was added to L_1 (0.05 g; 0.13 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) ν_{max} / 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, CD$_2$Cl$_2$) δ 9.22 (s, 1H, NH), 7.83 (dd, 2H, Ar-H), 7.79 (t, 1H, *J* 7.7 Hz, Ar-H), 7.69 (dd, 2H, *J* 7.7 Hz, Ar-H), 7.61 (t, 2H, *J* 7.7 Hz, Ar-H), 7.53 (t, 2H, *J* 7.7 Hz, Ar-H), 7.47 (t, 1H, *J* 7.7 Hz, Ar-H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 160.8, 151.0, 138.9, 132.6, 130,9, 130.5, 129.8, 126.7, 123.2; ^{19}F NMR (370 MHz, CD$_2$Cl$_2$) δ −132.5, −156.2, −163.4; ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) −3.78 ppm ($\nu^{1/2}$ ca. 800 Hz); anal. calcd. for C$_{31}$H$_{11}$BF$_{15}$N$_3$O: C, 50.50; H, 1.50; N, 5.70; found: C, 50.30; H, 1.56; N, 5.87.

N-(2,6-Diisopropylphenyl)-2-phenyldiazenecarboxamide-B(C$_6$F$_5$)$_3$ adduct (A$_2$)

This compound was obtained by the same procedure as for the synthesis of A_1, but with B(C$_6$F$_5$)$_3$ (0.09 g; 0.17 mmol) and L_2 (0.05 g; 0.17 mmol).

IR (KBr) ν_{max} / cm^{-1} 3336, 3068, 1646, 1595, 1541, 1518, 1468, 1380, 1316, 1287, 1103, 978, 782, 690, 679; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.61 (s, 1H, N-H), 7.78 (m, 3H, *J* 7.7 Hz, Ar-H), 7.61 (t, 2H, *J* 7.8 Hz, Ar-H), 7.48 (t, 1H, *J* 7.8 Hz, Ar-H), 7.30 (d, 2H, *J* 7.8 Hz, Ar-H), 2.99 (m, 2H, *J* 6.7 Hz, CH-iPr), 1.18 (d, 12H, *J* 6.7 Hz, CH$_3$); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 163.8, 151.3, 146.5, 138.7, 131.2, 130.8, 127.2, 126.5, 124.7, 29.2, 24.1; ^{19}F NMR

(370 MHz, CD$_2$Cl$_2$) δ −132.5, −157.0, −164.0; ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) −4.41 ppm ($\nu^{1/2}$ ca. 820 Hz); anal. calcd. for C$_{37}$H$_{23}$BF$_{15}$N$_3$O: C, 54.10; 2.82; N, 5.12; found: C, 53.80; 3.00; N, 5.23.

N-(2,6-Diisopropylphenyl)-2-(perfluorophenyl)diazene-carboxamide -B(C$_6$F$_5$)$_3$ adduct (A$_3$)

This compound was obtained by the same procedure as for the synthesis of A_1, but with B(C$_6$F$_5$)$_3$ (0.06 g; 0.13 mmol) and L_3 (0.05 g; 0.13 mmol).

IR (KBr) ν_{max} / cm^{-1} 3371, 2973, 2935, 1647, 1519, 1468, 1397, 1330, 1288, 1259, 1172, 1106, 1035, 980, 801, 678; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.49 (s, 1H, NH), 7.48 (t, 1H, *J* 7.8 Hz, Ar-H), 7.29 (d, 2H, *J* 7.8 Hz, Ar-H), 2.95 (m, 2H, *J* 6.8 Hz, CH-iPr), 1.15 (d, 6H, *J* 6.8 Hz, CH$_3$); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 163.1, 146.4, 127.1, 131.3, 124.8, 29.4, 23.7; ^{19}F NMR (370 MHz, CD$_2$Cl$_2$) δ −132.2, −132.9, −155.8, −156.7, −162.3, −163.1; ^{11}B NMR (160 MHz, CD$_2$Cl$_2$) −6.02 ppm ($\nu^{1/2}$ ca. 1100 Hz); anal. calcd. for C$_{37}$H$_{18}$BF$_{20}$N$_3$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

Compounds L_1, L_3 and A_3 crystallized with two molecules in the asymmetric unit. In all compounds (L_1, L_2, 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.[8,36] 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
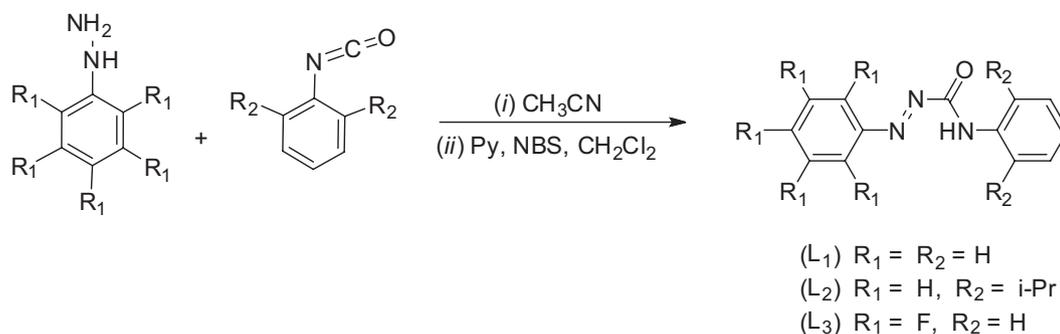
Scheme 1. Synthetic pathway to the diazenecarboxamide ligand.

Table 1. Selected spectroscopic parameters of the diazenecarboxamide ligands L_1, L_2, L_3, and the diazenecarboxamide-BCF adducts A_1, A_2 and A_3

	L_1	L_2	L_3	A_1	A_2	A_3
NMR δ^1H / ppm						
N–H	8.69	8.03	7.80	9.22	8.61	8.49
HC^{iPr}	–	3.19	3.16	–	2.99	2.95
Me^{iPr}	–	1.23	1.24	–	1.18	1.15
NMR $\delta^{13}C$ / 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

(NBS/Py) yields the desired compound. See Experimental and Supplementary Information (SI) sections.

The symmetric (L_1)[37] and asymmetric $(L_2$ and $L_3)$ diazenecarboxamide ligands were purified by crystallization in methanol, in 80, 52 and 49% yield, respectively. In each case the ^1H, ^{13}C NMR spectra (in $[D_2]$-dichloromethane) are consistent with the exclusive formation of one product. In the case of L_3, the three signals in the ^{19}F 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 L_1, L_2 and L_3, respectively, due to the C=O functionality.

Solid-state characterization of L_1 by single-crystal X-ray diffraction (Figure 3) is consistent with the structure in Scheme 1. Compound L_1 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.
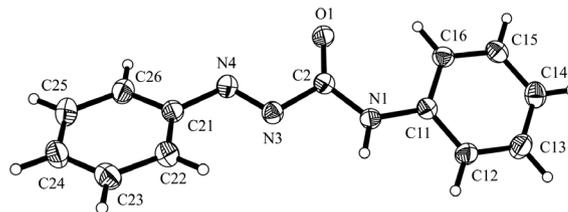
Figure 3. Molecular structure of the L_1 ligand. Only one of the two independent molecules found in the asymmetric unit is shown (thermal ellipsoids are shown at 30% probability).

Also, single crystals of L_2 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 L_2 shows that the N3–N4 bond is slightly out of the C2 sp^2 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 L_3 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 L_3

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

	L_1	L_2	L_3	A_1	A_2	A_3
Bond lengths (Å)						
O(1)-C(2)	1.217(2)	1.217(3)	1.217(2)	1.260(3)	1.262(2)	1.251(4)
N(1)-C(2)	1.338(2)	1.333(3)	1.321(3)	1.308(3)	1.309(3)	1.306(5)
N(3)-C(2)	1.466(2)	1.464(3)	1.462(3)	1.423(3)	1.432(3)	1.434(5)
N(3)-N(4)	1.246(2)	1.227(3)	1.233(2)	1.249(2)	1.252(2)	1.242(4)
O(1)-B(1)	–	–	–	1.565(3)	1.577(3)	1.593(5)
Bond Angles (°)						
O(1)-C(2)-N(1)	127.3(1)	126.8(2)	128.0(2)	121.7(2)	121.1(2)	121.3(3)
O(1)-C(2)-N(3)	124.4(1)	116.5(2)	118.0(2)	118.5(2)	118.8(2)	121.8(3)
O(1)-B(1)-C(41)	-	-	–	101.1(2)	111.0(2)	109.0(3)
O(1)-B(1)-C(51)	–	–	–	108.8(2)	106.0(2)	104.5(3)
O(1)-B(1)-C(61)	–	–	–	–	102.1(2)	101.9(3)
O(1)-B(1)-C(31)	–	–	–	109.3(2)	–	–
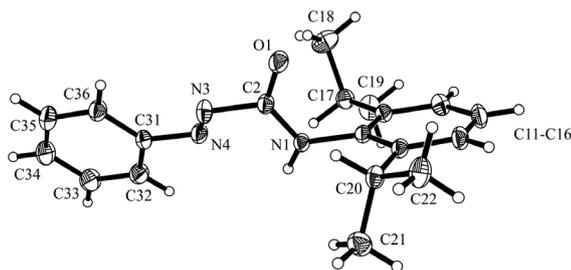
Figure 4. Molecular structure of the L_2 ligand (thermal ellipsoids are shown at 30% probability).

has a similar topology as L_2 (Figure 4). This can be seen in the N4–N3–C2–N1 dihedral angle (68.9(2)°) compared with L_2 (−31.0(4)°), as well as the angles around C2 (N3–C2–O1 and N1–C2–O1, which are 118.0(2)° and 128.0(2)°, respectively. This can also be observed in the N4–N3, C2–O1 and N3–C2, N1–C2 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.
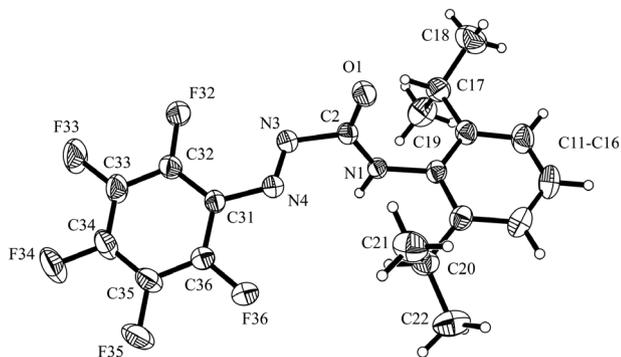
Figure 5. Molecular structure of the L_3 ligand. Only one of the two independent molecules found in the asymmetric unit is shown (thermal ellipsoids are shown at 30% probability).

Reaction of the diazenecarboxamide ligand with $B(C_6F_5)_3$

We decided to investigate the diazenecarboxamide ligand's affinity for $B(C_6F_5)_3$ by stirring of the reaction mixture of the respective ligand (L_1-L_3) plus one equivalent of $B(C_6F_5)_3$ for 2 h at RT in dichloromethane (DCM), eventually yielding adduct A_1-A_3 [i.e., L_1-$B(C_6F_5)_3$] 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 N4−N3−C2−N1 is −16.8(3)°). The internal bonding situation is found to be asymmetric. The N3−N4 bond (1.249(2) Å) is markedly shorter than the opposite N3−C2 and N1−C2 bonds, 1.423(3) and 1.308(3) Å, and consequently the C2−O1 bond (1.260(3) Å) is shorter and consistent with a double bond character.

Carbon atom C2 is trigonal planar (sum of the bond angles at C2 360.0°). The $B(C_6F_5)_3$ 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)° (O1−B1−C31), 101.1(2)° (O1−B1−C41), and 108.8(2)° (O1−B1−C51). The C2−O1−B1 unit has a bent molecular geometry (angles C2−O1−B1 131.5(2)°. The O1−B1 bond length (1.565(3) Å) is within the typical O−B single bond range.[38-40] The C2−O1 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 C=O stretching band at $\tilde{v} = 1646$ cm^{-1}, which is shifted by $\tilde{v} = 54$ cm^{-1} to lower wavenumber compared to its parent L_1
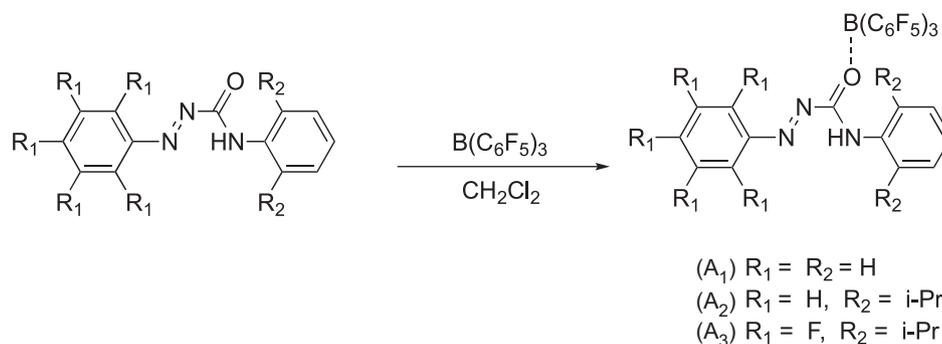
Scheme 2. Synthetic pathway to the diazenecarboxamide-B(C_6F_5)$_3$ adduct.
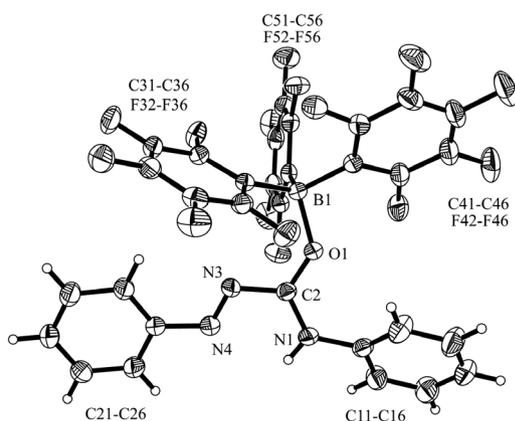
Figure 6. Molecular structure of the A$_1$ adduct (thermal ellipsoids are shown at 30% probability).
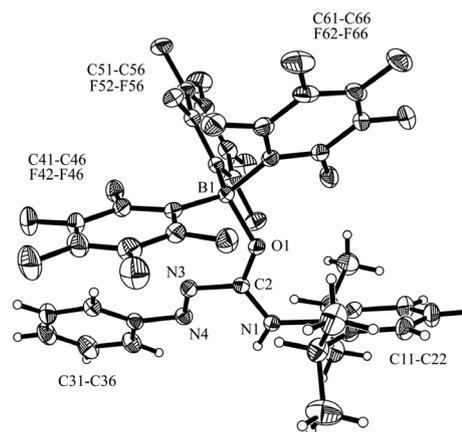
Figure 7. Molecular structure of the A$_2$ adduct (thermal ellipsoids are shown at 30% probability).

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 δ 9.22 ppm (in [D$_2$]-dichloromethane) is observed. The ^{11}B NMR spectrum features a typical four-coordinate boron resonance (δ −3.78 ppm), which is supported by a characteristically small $\Delta\delta$ (*p,m*) C_6F_5 chemical shift difference[41-44] in the ^{19}F NMR spectrum [δ −132.5 (*o*), −156.2 (*p*), −163.4 (*m*)]. Adduct A$_1$ shows a characteristic ^{13}C resonance for the C=O--B units (δ ^{13}C: 168.8 ppm).

Treatment of L$_2$ with one molar equivalent of B(C_6F_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_6F_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)° (O1−B1−C41), 106.0(2)° (O1−B1−C51), and 102.1(2)° (O1−B1−C61). The O1−B1 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 $\tilde{v}$ = 1648 cm^{-1}, which is shifted by $\tilde{v}$ = 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: δ 8.61 −NH; ^{13}C: δ 164.2, (C=O---)] are observed. The ^{11}B NMR spectrum features a typical four-coordinate boron resonance (δ −4.41 ppm), and the

^{19}F NMR signals at δ −132.5 (*o*), −157.0 (*p*), and −164.0 (*m*) for the C_6F_5 substituents on boron.

Finally, the addition of one molar equivalent of $B(C_6F_5)_3$ to L_3 in DCM at RT (2 h) also led to complete conversion to A_3, 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_3 is coordinated by $B(C_6F_5)_3$, (O1−B1 1.593(5) Å, angles O1−B1−C41 109.0(3)°, O1−B1−C51 105.5(3)°, O1−B1−C61 101.9(3)°). 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).
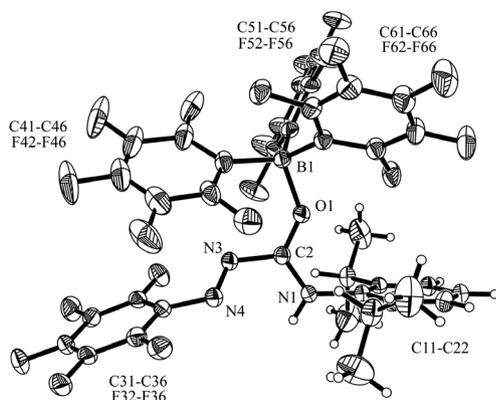
Figure 8. Molecular structure of the A_3 adduct. Only one of the two independent molecules found in the asymmetric unit is shown (thermal ellipsoids are shown at 30% probability).

In solution, compound A_3 has a ^{13}C NMR signal for the carbonyl carbon atom (C2) at δ 162.8 ppm. As expected, a single set of C_6F_5 resonances at δ −132.9 (*o*), −156.7 (*p*), and −163.1 ppm (*m*) was observed for the $B(C_6F_5)_3$ group coordinated with the carbonyl function (Scheme 2), and the corresponding ^{11}B NMR resonance was found at −6.02. The C_6F_5 ring produced a single set of *o*-, *p*- and *m*- ^{19}F NMR resonances at δ −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-$B(C_6F_5)_3$ adduct has been isolated and fully characterized. The binding of $B(C_6F_5)_3$ 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.

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