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Synthesis of new 2,3-perfluoroalkyl- and perfluoroaryl-1,4-diazabutadienes (α-diimines)

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Abstract

Reaction of either decafluorobenzil or perfluorobiacetyl with two equivalents of Li[N($SiMe_3$)$_2$], followed by quenching with $ClSiMe_3$, provides *N,N′*-bis(trimethylsilyl)-1,2-bis(pentafluorophenyl)ethanediimine **1** and *N,N′*-bis(trimethylsilyl)-1,1,1,4,4,4-hexafluoro-2,3-butanediimine **2**, respectively. These represent the first examples of perfluoroalkyl- and perfluoroaryl-substituted diazabutadienes. Both compounds have been characterized based on ^{13}C NMR, IR, elemental analysis and, for **1**, single crystal X-ray crystallographic structure determination. Compound **1** crystallizes in the *C2/c* space group, with a=20.3203(9) X, b=6.0758(3) X, c=19.7948(9) X, α=90°, β=106.2903(7)°, γ=90°.

Keywords: diimines; diones; halogens; halogen compounds; *N*-imides.

1,4-Diazabutadienes (α-diimines) have been examined extensively over the last two decades as ligand systems for: (i) their variety of coordination modes and reactivity of their coordination complexes;[1] (ii) the applications of such complexes in organic synthesis and catalysis;[2] and (iii) the utilization of such complexes as luminescence labels for detection and photochemical cleavage of DNA.[3] In addition, we have recently reported on the utilization of selected α-diimines[4] in dehalosilylation/ring-closure reactions with $SbCl_3$ or $BiCl_3$, to provide the first examples of Sb- and Bi-containing 1,2,5-pnictadiazoles.[5] One of the most appealing attributes of the diazabutadienes, which plays a significant role in the physical and chemical properties of the resultant coordination compounds,[1–3] is their strong π-acceptor ability as a result of the energetically low-lying LUMO.[6] To date, however, there are no reported examples of 2,3-perfluoroalkyl- or perfluoroaryl-substituted 1,4-diazabutadienes. Such systems would be expected to possess even lower-lying LUMOs and, consequently, be even stronger π-acceptor ligands. Their utility in the synthesis of new perfluoroalkyl- or perfluoroaryl-substituted heterocycles is also unexplored.

We report herein the convenient high-yield synthesis of two perfluoroalkyl/aryl-substituted α-diimines, *N,N′*-bis(trimethylsilyl)-1,2-bis(pentafluorophenyl)ethanediimine **1** and *N,N′*-bis(trimethylsilyl)-1,1,1,4,4,4-hexafluoro-2,3-butanediimine **2**. Characterization of these new diimines was accomplished

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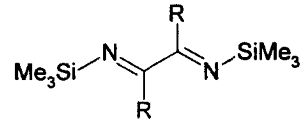
by ^1H and ^{13}C NMR, IR, elemental analysis and, for **1**, single crystal X-ray crystallographic structure determination.



1; R = -C_6F_5

2; R = -CF_3

Syntheses of **1** and **2** were accomplished in a manner analogous to our previously reported synthesis of phenanthrenequinone-(9,10)-bis(trimethylsilyl)diimine and *N,N'*-bis(trimethylsilyl)-1,2-diphenylethanediimine;[5] namely, via addition of two equivalents Li[N(SiMe$_3$)$_2$] to the precursor α-diones, decafluorobenzil and perfluorobiacetyl, respectively, followed by ClSiMe$_3$ quench.[7] Decafluorobenzil was synthesized via the addition of the corresponding lithium diarylcuprate to oxalyl chloride, and perfluorobiacetyl was synthesized via $CrO_3/H_2SO_4 \cdot xSO_3$ oxidation of *cis/trans*-1,1,1,4,4,4-hexafluoro-2,3-dichloro-2-butene.[8]

The ^{13}C NMR, IR and mass spectral (in the case of **2**) data are all consistent with the α-diimine structures.[7,9] In addition, **1** has been further characterized by single crystal X-ray diffraction structure determination, and the molecular structure is illustrated (with 30% thermal ellipsoids) in Fig. 1.[10] Inspection of the X-ray diffraction data reveals a number of features that serve to define these new α-diimines. The molecule lies on a crystallographic inversion center. The carbon nitrogen bond length is 1.246 Å, characteristic of C=N double bonds as found in oximes and imines.[11] The angles around C(1) sum to

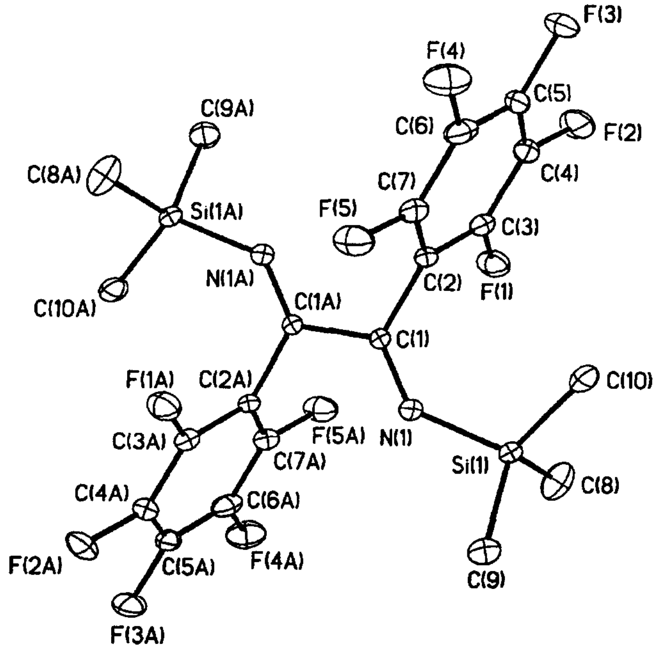


Figure 1. Molecular structure of $[Me_3SiN{=}C(C_6F_5)]_2$, with 30% thermal ellipsoids, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(1A) 1.515(8), C(1)–N(1) 1.246(6), C(1)–C(2) 1.516(6), N(1)–SI(1) 1.754(4), N(1)–C(1)–C(2) 126.4(4), N(1)–C(1)–C(1A) 120.9(5), C(2)–C(1)–C(1A) 112.6(5)

359.9°, as expected for an sp^2 hybridized carbon. As required by the imposed crystallographic symmetry, the N(1)–C(1)–C(1A)–N(1A) torsion angle is zero; the N(1)–C(1)–C(1A)–C(2A) torsion angle is 2.1°. The angle between the plane of the pentafluorophenyl ring and the N(1)–C(1)–C(1A)–N(1A) plane is approximately 103°.

As mentioned, one attribute of the diazabutadienes that plays a significant role in the physical and chemical properties of the resultant coordination compounds, is their strong π-acceptor ability as a result of the energetically low-lying LUMO. We have performed semi-empirical molecular orbital calculations to estimate the relative HOMO/LUMO energies for the two new α-diimines reported herein, as well as selected non-fluorinated analogues for comparison.[12] The results of these calculations are illustrated in Fig. 2. Relative to 9,10-phenanthrenequinonediimine, the new diimines **1** and **2** are 0.53 eV and 0.26 eV lower in energy, respectively.

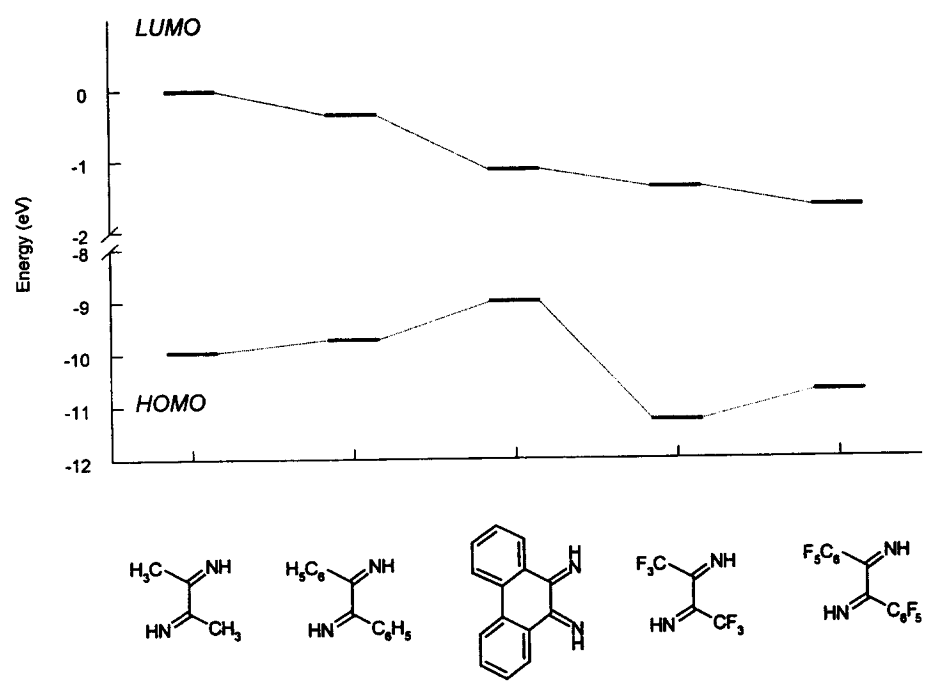
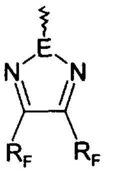


Figure 2. Relative HOMO/LUMO energies for selected α-diimines (diazabutadienes), resulting from PM3 geometry optimization and single point energy calculations

These new diimines should find application in the preparation of a variety of novel and potentially useful metallodiimines and heterocycles. For example, analogous to our previous report,[5] reactions of these new diimines with polyhaloelement (EX_n, E=Main Group element) compounds provide convenient access to a wide variety of 4,5-bis(R_F)-1,3,2-diazaheteroles (R_F=-CF_3, C_6F_5) **3**. We have recently reported on reactions of **2** with $GaBr_3$, InI_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, $SeBr_4$, and $TeBr_4$ to yield the corresponding 4,5-bis(trifluoromethyl)-1,3,2-diazaheteroles, and the chemical and physical properties of these novel Main Group element-containing heterocycles.[13]



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Finally, in related work, we have also prepared the analogous (non-silylated) 1,2-di(pentafluorophenyl)-ethanediimine, H-N=C(C_6F_5)-(C_6F_5)C=N-H, and 1,1,1,4,4,4-hexafluoro-2,3-butanediimine, H-N=C(CF_3)-(CF_3)C=N-H, via [(η^5-C_5H_5)$_2$TiCl]$_2$-mediated reductive coupling of pentafluorobenzonitrile and trifluoroacetonitrile, respectively.[14]

Acknowledgements

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7. (a) *N,N'*-bis(trimethylsilyl)-1,2-bis(pentafluorophenyl)ethanediimine (**1**): To a suspension of 19.0 g (48.7 mmol) of decafluorobenzil, $C_6F_5C(O)C(O)C_6F_5$, in 500 mL of anhydrous cyclohexane was added dropwise, at 5–10°C, 16.3 g (97.4 mmol) of LiN[Si(CH_3)$_3$]$_2$. After addition was complete, the reaction was refluxed for 8 h. The reaction was then cooled to 5–10°C and 13 mL (102 mmol) ClSi(CH_3)$_3$ was added via syringe. The reaction was stirred overnight at room temperature, followed by 6 h at 65°C. The dark red solution was cooled to room temperature and filtered through Celite® to remove LiCl, and the solvent removed in vacuo. The residue was re-dissolved in 200 mL of hot anhydrous hexane, and then cooled to −78°C). Approximately 11 g (21 mmol, 43%) of crystalline product, *N,N'*-bis(trimethylsilyl)-1,2-bis(pentafluorophenyl)ethanediimine (**1**), was isolated by filtration. ^{13}C NMR (δ; CD_2Cl_2) 158.3 ppm (>C=N-, s), 143.5 (dm, J^1=244.4 Hz), 141.6 (dm, J^1=253.3 Hz), 137.6 (dm, J^1=253.7 Hz), 114.8 ppm (*ipso* C, t, J^2=22.9 Hz), −1.1 ppm [-Si(CH_3)$_3$]. Infrared (C_6H_6) $\nu_{C=N}$=1685, 1696 cm^{-1}. Elemental analysis: calcd (found) for $C_{20}H_{18}N_2F_{10}Si_2$: C, 45.11% (45.33%), H, 3.41% (3.52%), N, 5.26% (5.19%). (b) *N,N'*-bis(trimethylsilyl)-1,2-bis(trifluoromethyl)ethanediimine (**2**): 80.0 gm (412 mmol) of perfluorobiacetyl, $F_3CC(O)C(O)CF_3$, was dissolved in 500 mL of anhydrous hexane, and cooled to −78°C. Using a vented addition funnel, 142 gm (825 mmol) LiN[Si(CH_3)$_3$]$_2$, dissolved in 300 mL anhydrous hexane, was added dropwise. After the addition was complete, the mixture was allowed to warm to room temperature and stirred overnight. The mixture was then refluxed for 6 h, and then cooled back to room temperature. To the homogeneous reaction mixture was added, via syringe, approximately 115 mL (900 mmol) ClSi(CH_3)$_3$. The mixture was then stirred overnight at room temperature. The mixture was then heated to and stirred at 60°C for approximately 6 h. The mixture was then cooled to room temperature and filtered through Celite®. The hexane was removed, via atmospheric pressure distillation, and the remaining product mixture was vacuum distilled at 25–26°C/400–450 mtorr to yield 86.7 g (63%) of *N,N'*-bis(trimethylsilyl)-1,1,1,4,4,4-hexafluoro-2,3-butanediimine, (CH_3)$_3$Si-N=C(CF_3)-(CF_3)C=N-Si(CH_3)$_3$, (**2**). Elemental analysis: calcd (found) for $C_{10}H_{18}N_2F_6Si_2$: C, 35.70% (35.83%), H, 5.39% (5.42%), N, 8.33% (8.29%). ^{13}C[^{1}H] NMR (δ; CD_2Cl_2) 155.4 ppm (>C=N-, q, J^2=36.3 Hz), 116.9 ppm (-CF_3, q, J^1=286.7 Hz), 1.4 ppm [-Si(CH_3)$_3$, s]. Infrared

$\nu_{C=N}$=1714, 1716 cm^{-1}. Mass spectral analysis results (EI, 70 eV) [*m/e* (species, relative abundance %)]: 336 (M$^+$, 0.25), 168 (M$^+$/2, 23.10), 73 [-Si(CH$_3$)$_3$, 100].

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