Facile routes to Alkyl-BIAN ligands

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The Alkyl-BIAN ligands *tert*-Butyl-BIAN and 1-Adamantyl-BIAN have been synthesized and their structures have been determined by single-crystal X-ray diffraction along with that of the $ZnCl_2$ complex of *tert*-Butyl-BIAN.

The bis(arylimino)acenaphthene (Aryl-BIAN) class of ligands (Chart 1) can be construed as arising from the fusion of naphthalene and 1,4-diaza-1,3-butadiene (DAB) moieties. One of the consequences of this hybrid character is that Aryl-BIAN ligands can function as both electron and proton sponges. Not unexpectedly, this desirable and versatile combination of properties has attracted the attention of the catalysis community and, as a consequence, several Aryl-BIAN-supported transition metal complexes have emerged as catalysts for enabling a variety of important chemical transformations.[1] Given the foregoing, in conjunction with the almost ubiquitous use of the *tert*-Butyl-DAB ligand in p-, d- and f-block chemistry,[2] it is at first blush surprising that *e.g.* the analogous *tert*-Butyl-BIAN ligand remains unreported. Some of the obstacles confronting the synthesis of Alkyl-BIAN ligands have, in fact, been addressed previously. Thus Ragaini *et al.*[3] correctly drew attention to the ring strain in the five-membered BIAN ring that is due to the fact that all five carbon atoms adopt sp^2 hybridization. To thwart the tendency towards the relief of ring strain *via* isomerization, these authors adopted the strategy of employing nitrogen substituents with even more strain than the C_5 BIAN ring itself, namely cyclopropyl groups. The same authors attributed their failure to prepare *tert*-Butyl-BIAN (**1**) and 1-Adamantyl-BIAN (**2**) by the classical route of treating acenaphthenequinone with the respective primary amine or *via* a transimination procedure to insurmountable steric effects.[3] Moreover, attempts to prepare BIAN ligands with smaller alkyl groups such as *n*-Bu and $PhCH_2$ were forestalled by the presence of α-hydrogen atoms which resulted in isomerization and subsequent decomposition.[3,4] Herein we describe convenient syntheses of **1** and **2** using iminoalane and aminoalane transfer reagents, respectively. Both new Alkyl-BIAN ligands have been structurally authenticated, as has the $ZnCl_2$ complex of **1**.

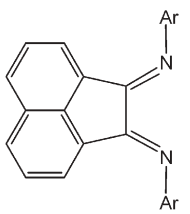

Chart 1

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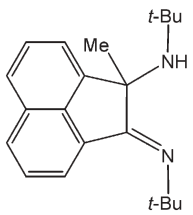
Amino-[5] and iminoalanes[6] have been employed successfully for the transfer of imido moieties. Specifically, it has been shown that aminoalane dimers of the type $[Me_2Al\text{-}\mu\text{-}N(H)R]_2$ (R = fluoroaryl)[5] are effective reagents for the conversion of C=O into C=NR functionalities. Accordingly, our first attempt to prepare **1** involved the treatment of acenaphthenequinone with an excess of $[Me_2Al\text{-}\mu\text{-}N(H)(t\text{-}Bu)]_2$ (**3**)[7] in toluene solution. Following hydrolytic work-up of the reaction mixture and purification, **4** was isolated in >50% yield.



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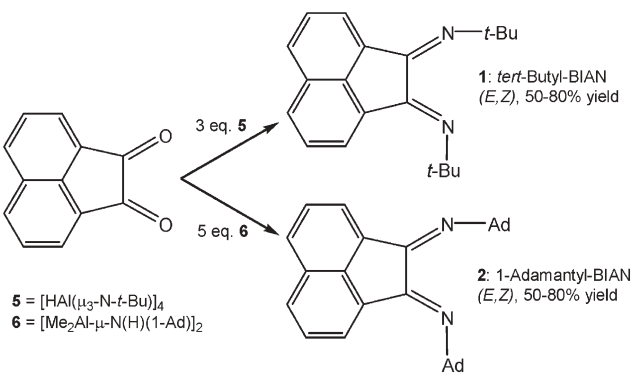
However, compound **4** was identified as an imino–amino derivative rather than the desired diimine on the basis of NMR and mass spectroscopic data.[8] Assuming that the source of the Me group in **4** is the aminoalane **3**,[9] the obvious next step was to employ a transfer agent that lacked Al–Me groups. The iminoalane cubane $[HAl(\mu_3\text{-}N\text{-}t\text{-}Bu)]_4$ (**5**)[10] seemed ideal for this purpose and treatment of acenaphthenequinone with three equivalents of **5** in toluene solution afforded the desired *tert*-Butyl-BIAN ligand (**1**) as a yellow crystalline solid in yields of 5 0–80% (Scheme 1). Satisfactory spectroscopic data were acquired for **1**[11] and the molecular structure was determined by single-crystal X-ray diffraction.[12] An interesting feature of the structure of **1** (Fig. 1) is the fact that it exists in the (*E*,*Z*) isomeric form in contrast to Aryl-BIAN ligands[4,13] which, with one exception,[14]



Scheme 1

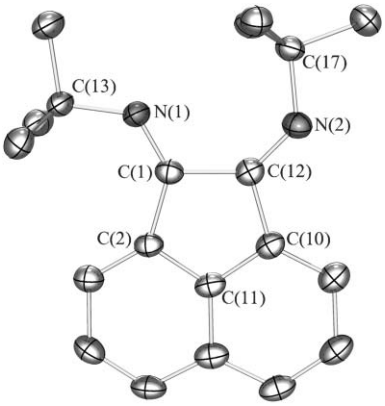


Fig. 1 View of the *tert*-Butyl-BIAN ligand (**1**) showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): C(1)–N(1) 1.282(3), C(12)–N(2) 1.274(4), C(1)–C(12) 1.551(4), C(1)–C(2) 1.496(4), C(2)–C(11) 1.426(4), C(11)–C(10) 1.407(4), C(10)–C(12) 1.481(4); C(13)–N(1)–C(1) 126.9(2), N(1)–C(1)–C(12) 118.8(2), C(1)–C(12)–N(2) 135.3(3), C(12)–N(2)–C(17) 129.5(3), C(2)–C(1)–C(12) 106.2(2), C(1)–C(12)–C(10) 105.3(2), C(12)–C(10)–C(11) 108.7(2), C(10)–C(11)–C(2) 112.8(2), C(11)–C(2)–C(1) 106.9(2).

exist as (*E*,*E*) isomers in the crystalline state.[15] These differences in isomeric preference evidently arise from a complex interplay of the steric demands of the imino substituents, lone pair–lone pair repulsions between imino-nitrogen lone pairs and crystal packing effects.

In contrast to the reaction of acenaphthenequinone with $[Me_2Al\text{-}\mu\text{-}N(H)(t\text{-}Bu)]_2$ which gave **4**, the corresponding reaction with five equivalents of $[Me_2Al\text{-}\mu\text{-}N(H)(1\text{-}Ad)]_2$ (**6**)[17] in toluene solution afforded, following work-up of the reaction mixture, >50% yields of yellow, crystalline 1-Adamantyl-BIAN (**2**) (Scheme 1). Compound **2** was characterized by spectroscopic methods[11] and X-ray analysis.[12] Like **1**, the 1-adamantyl analogue, **2** exhibits the (*E*,*Z*) isomeric preference in the crystalline state (Fig. 2). The metrical parameters for **1** and **2** are very similar to, but distinguished from, those of Aryl-BIAN ligands with (*E*,*E*) geometries. In contrast to the latter, there is considerable disparity in the C–N–C and N–C–C bond angles at N(1) and N(2) in **1** and **2** (see Fig. 1 and 2 captions). Finally, the $ZnCl_2$ complex of *tert*-Butyl-BIAN (**7**) was prepared in ~90% yield *via* the reaction of **1** with $ZnCl_2$ in THF solution, followed by recrystallization from MeCN solution. An X-ray crystallographic study of **7**[12] (Fig. 3) revealed that, despite the (*E*,*Z*) to (*E*,*E*) isomeric conversion that accompanies ligation to the zinc atom, the BIAN bond distances for **7** are virtually identical to those of the free *tert*-Butyl-BIAN ligand.

In conclusion, we have prepared and structurally characterized Alkyl-BIAN ligands that are analogous to the well-known DAB ligand class. Given the differences in stereoelectronic properties of alkyl and aryl substituents, it is anticipated that the new Alkyl-BIAN ligands will find wide use in coordination chemistry and catalysis.

We are grateful to the Petroleum Research Fund (Grant 38970-AC1), the National Science Foundation (Grant CHE-0240008) and the Robert A. Welch Foundation (F-0003) for financial support.

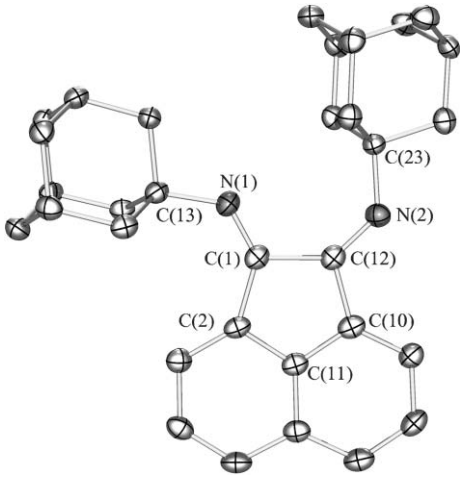


Fig. 2 View of the 1-Adamantyl-BIAN ligand (**2**) showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°): C(1)–N(1) 1.270(4), C(12)–N(2) 1.272(4), C(1)–C(12) 1.567(4), C(1)–C(2) 1.516(4), C(2)–C(11) 1.422(4), C(11)–C(10) 1.401(4), C(10)–C(12) 1.491(4); C(13)–N(1)–C(1) 127.8(3), N(1)–C(1)–C(12) 118.5(3), C(1)–C(12)–N(2) 136.2(3), C(12)–N(2)–C(23) 130.3(3), C(2)–C(1)–C(12) 105.1(3), C(1)–C(12)–C(10) 105.1(3), C(12)–C(10)–C(11) 109.1(3), C(10)–C(11)–C(2) 113.1(3), C(11)–C(2)–C(1) 107.4(3).

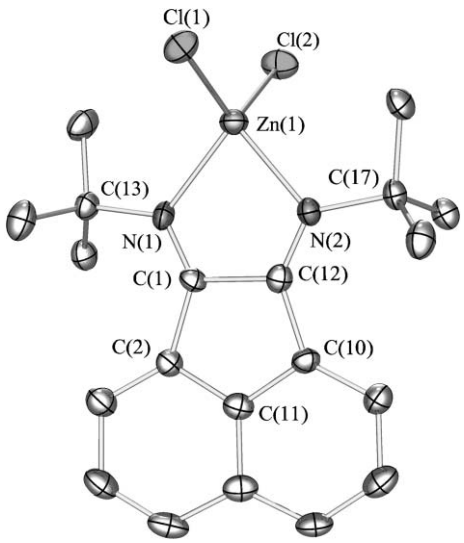


Fig. 3 View of (*tert*-Butyl-BIAN)$ZnCl_2$ (**7**) showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms and CH_3CN of crystallization omitted for clarity). Selected bond distances (Å) and angles (°): Zn(1)–N(1) 2.083(3), Zn(1)–N(2) 2.078(3), Zn(1)–Cl(1) 2.219(1), Zn(1)–Cl(2) 2.225(1), C(1)–N(1) 1.278(4), C(12)–N(2) 1.267(4), C(1)–C(12) 1.549(5), C(1)–C(2) 1.496(5), C(2)–C(11) 1.414(4), C(11)–C(10) 1.417(5), C(10)–C(12) 1.477(5); N(1)–Zn(1)–N(2) 81.42(11), Cl(1)–Zn(1)–Cl(2) 118.44(4), C(13)–N(1)–C(1) 125.7(3), N(1)–C(1)–C(12) 117.0(3), C(1)–C(12)–N(2) 116.8(3), C(1)–C(12)–N(2) 116.8(3), C(12)–N(2)–Zn(1) 121.1(2), C(12)–N(2)–C(17) 126.4(3), C(2)–C(1)–C(12) 105.9(3), C(1)–C(12)–C(10) 105.9(3), C(10)–C(11)–C(2) 114.4(3), C(11)–C(2)–C(1) 105.9(3).

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11 *Spectroscopic data* for **1**: ^{1}H NMR (C_6D_6) δ 1.49 (s, 9H, *t*-Bu), 1.91 (s, 9H, *t*-Bu), 7.19 (d of d, 1H, J = 7.2 Hz, NapC–H), 7.32 (d of d, 1H, J = 7.5 Hz, NapC–H), 7.51 (d, 2H, J = 7.5 Hz, NapC–H), 7.69 (d, 1H, J = 7.5 Hz, NapC–H), 8.11 (d, 1H, J = 8.11 Hz, NapC–H). MS (CI^+, CH_4): *m*/*z* (100%, 293, M + H^+); HRMS (CI^+, CH_4) calc. for $C_{20}H_{25}N_2$, 293.2018; found, 293.2023. Spectroscopic data for **2**: ^{1}H NMR (THF-d_8): δ 1.11–1.55 (CH_2, Ad), 2.30–2.50 (CH, Ad), 7.88 (d of d, 1H, J = 7.5 Hz, NapC–H), 7.93 (d of d, 1H, J = 7.8 Hz, NapC–H), 8.05 (d, 1H, J = 6.6 Hz, NapC–H), 8.16 (d, 1H, J = 8.1 Hz, NapC–H), 8.22 (1H, J = 8.4 Hz, NapC–H), 8.44 (d, 1H, J = 7.2 Hz, NapC–H). MS (CI^+, CH_4): *m*/*z* (100%, 449, M + H^+); HRMS (CI^+, CH_4) calc. for $C_{32}H_{37}N_2$ 449.2957; found, 449.2955. Spectroscopic data for **7**: ^{1}H NMR (CD_2Cl_2): δ 1.90 (s, 18H, *t*-Bu), 7.91 (d of d, 2H, J = 8.0 Hz, NapC–H), 8.25 (d, 2H, J = 7.8 Hz, NapC–H), 8.44 (d, 2H, NapC–H). MS (CI^+, CH_4): *m*/*z* (100%, 428, M + H^+); HRMS (CI^+, CH_4) calc. for $C_{20}H_{24}Cl_2N_2Zn$, 426.0608; found, 426.0607.

12 *Crystal data* for **1**: $C_{20}H_{24}N_2$, tetragonal, $P43$, a = 10.986(5), b = 10.986(5), c = 13.853(5) Å, V = 1672.0(1) Å^3, Z = 4, D_c = 1.162 g cm^{-3}, μ(Mo-Kα) = 0.068 mm^{-1}, T = 153(2) K, 1986 independent reflections (R_{int} = 0.0438), final R indices (206 parameters) for 1986 independent reflections [$I > 2\sigma(I)$] are R_1 = 0.0465, wR_2 = 0.1008, GOF = 1.082. For **2**: $C_{32}H_{36}N_2$, triclinic, $P\bar{1}$, a = 9.965(5), b = 11.003(5), c = 11.964(5) Å, α = 92.589(5), β = 105.670(5), γ = 108.860(5)°, V = 1182.5(9) Å^3, Z = 2, D_c = 1.260 g cm^{-3}, μ(Mo-Kα) = 0.073 mm^{-1}, T = 153(2) K, 5361 independent reflections (R_{int} = 0.0746), final R indices (307 parameters) for 5361 independent reflections [$I > 2\sigma(I)$] are R_1 = 0.0595, wR_2 = 0.1194, GOF = 0.958. For **7**: $C_{22}H_{27}Cl_2N_3Zn$ (**7**·CH_3CN), monoclinic, space group Cc, a = 11.276(5), b = 20.656(5), c = 9.430(5) Å, β = 93.968(5)°, V = 2191.1(2) Å^3, Z = 4, D_c = 1.424 g cm^{-3}, μ(Mo-Kα) = 1.377 mm^{-1}, T = 153(2) K, 4350 independent reflections, (R_{int} = 0.0106), final R indices (261 parameters) for 4350 independent reflections [$I > 2\sigma(I)$] are R_1 = 0.0374, wR_2 = 0.0707, GOF = 1.068. CCDC: 605399 (**1**), 605400 (**2**) and 605401 (**7**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606390j.

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15 In solution, Aryl-BIAN ligands have been shown to undergo facile interconversion between the (*E*,*E*) and (*E*,*Z*) isomers.[4,16] We have found recently that the crystalline state of *ortho*-$CF_3C_6H_4$-BIAN[16] comprises an equimolar mixture of (*E*,*E*) and (*E*,*Z*) isomers. *Crystal data* for $C_{26}H_{14}F_6N_2$, monoclinic, $P2_1/c$, a = 21.339(5), b = 11.819(5), c = 16.806(5) Å, β = 90.076(5)°, V = 4239(2) Å^3, Z = 8, D_c = 1.468 g cm^{-3}, μ(Mo-Kα) = 0.124 mm^{-1}, T = 153(2) K, 9114 independent reflections (R_{int} = 0.0579), final R indices (613 parameters) for 9114 independent reflections [$I > 2\sigma(I)$] are R_1 = 0.0597, wR_2 = 0.1691, GOF = 1.009. CCDC 606233.

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