Synthesis and reactivity of tetrakis(imino)pyracene (TIP) ligands; bifunctional analogues of the BIAN ligand class†

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Received (in Austin, TX, USA) 14th December 2007, Accepted 28th January 2008
First published as an Advance Article on the web 3rd March 2008
DOI: 10.1039/b719251g

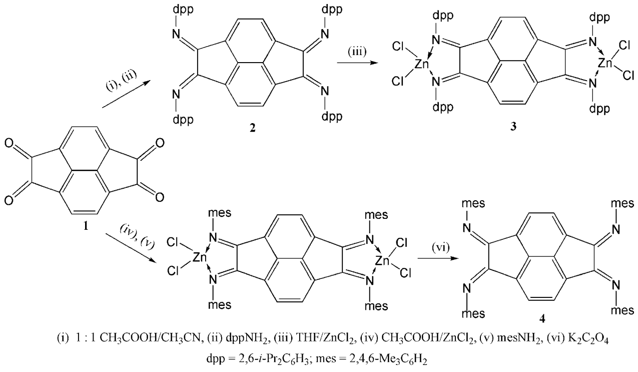
The first two examples of a new class of bifunctional BIAN-type ligand have been prepared, and the reactions of one such ligand with $CuBr_2$ and BCl_3 have been explored.

The bis(imino)acenaphthene (BIAN) ligand class can be regarded as originating from the fusion of a naphthalene ring and a 1,4-diaza-1,3-butadiene moiety. The rigidity of the resulting ligands make them excellent platforms for the support of, *e.g.*, late transition metal complexes that serve as robust catalysts for a significant number of useful transformations.[1] Further interest in the BIAN ligand class has arisen from their ability to function as both electron and proton sponges. Given the foregoing desirable properties, we became interested in developing a BIAN-type ligand that features the fusion of two 1,4-diaza-1,3-butadiene moieties to the naphthalene ring. It was envisioned that such bifunctional BIAN ligands could serve as, *e.g.*, redox-active links for supramolecular construction, molecular wire models, metallopolymers and bimetallic catalyst supports. Herein, we describe (i) the first two examples of the tetrakis(imino)pyracene (TIP) ligand class, (ii) the first example of a polymer featuring a BIAN-type ligand and (iii) the use of a new TIP ligand for the generation of a dinuclear boron dication.

As summarized in Scheme 1, two approaches were taken to synthesize the target TIP ligands. Both methods started with 1,2,5,6-tetraketopyracene (**1**).[2] Treatment of **1** with a 1 : 1 mixture of CH_3COOH and CH_3CN at 80 °C, followed by the addition of five equivalents of 2,6-i-$Pr_2C_6H_3NH_2$ and reflux of the reaction mixture, resulted in a 90% yield of the 2,6-diisopropylphenyl-substituted TIP ligand, **2**, which, in turn, was converted into the corresponding bis($ZnCl_2$) complex, **3**, *via* reaction with excess $ZnCl_2$ in a THF solution. The bis($ZnCl_2$) complex of the mesityl-substituted TIP ligand was generated as an intermediate by the treatment of **1** with a $ZnCl_2$/acetic acid mixture, followed by reaction with 2,4,6-$Me_3C_6H_2NH_2$. The free mesityl-substituted TIP ligand, **4**, was isolated in 50% overall yield by the decomplexation of this intermediate with potassium oxalate in a CH_2Cl_2/H_2O solution.

Satisfactory spectroscopic data were acquired for the two TIP ligands, **2** and **4**, as well as for the bis($ZnCl_2$) dpp-TIP complex, **3**.[3] Compounds **2**–**4** were also characterized by single-crystal X-ray diffraction.[4] Molecules of **2** are located on an inversion center, and the asymmetric unit of **3** contains two independent half molecules, each of which is located on an independent inversion center. The structures of TIP ligands **2** and **4** are very similar to each other. Within experimental error, the fused ring systems of **2** and **4** are planar. The torsion angle of the N═C–C═N fragment is 6.15° in **2**, and the corresponding value for **4** averages 5.75°. The average dihedral angles between the aryl substituents and the naphthalene moieties are 83.24 and 86.84° for **2** and **4**, respectively.

A solution of two equivalents of $CuBr_2$ in EtOH was layered on top of a THF solution of one equivalent of **2**. Crystals of the coordination polymer $[BrCu(dpp\text{-}TIP)CuBr]_n$ (**5**) formed slowly over a period of ~1 week. Polymer **5** was characterized by ^1H NMR spectroscopy, mass spectrometry[3] and single-crystal X-ray diffraction.[4] A prominent peak in the CI^+ mass spectrum occurs at m/z 1156, corresponding to the monomeric unit [BrCu(dpp-TIP)CuBr]. The crystal structure features essentially planar Cu(dpp-TIP)Cu moieties and Cu_2Br_2 rhomboids that are arranged in an approximately orthogonal fashion along the polymer chain (Fig. 1). It is clear from the composition of **5** that polymer formation is accompanied by the reduction of $CuBr_2$ to CuBr. There is, however, no evidence of redox activity within the TIP ligand. Thus, the C(1)–N(1) and C(5)–N(2) distances, which average 1.275(7) Å, correspond to C═N bonds and the C(1)–C(5) separation of 1.504(8) Å falls in the C–C single bond range. Even though the Cu–Br–Cu angle in the Cu_2Br_2 rhomboid is quite acute (68.06(3)°), the Cu···Cu distance of 2.7178(14) Å exceeds the



(i) 1 : 1 CH_3COOH/CH_3CN, (ii) $dppNH_2$, (iii) THF/$ZnCl_2$, (iv) $CH_3COOH/ZnCl_2$, (v) $mesNH_2$, (vi) $K_2C_2O_4$
dpp = 2,6-i-$Pr_2C_6H_3$; mes = 2,4,6-$Me_3C_6H_2$

Scheme 1

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† CCDC 670789 (**2**), 670790 (**3**), 670788 (**4**), 670791 (**5**) and 670787 (**6**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719251g

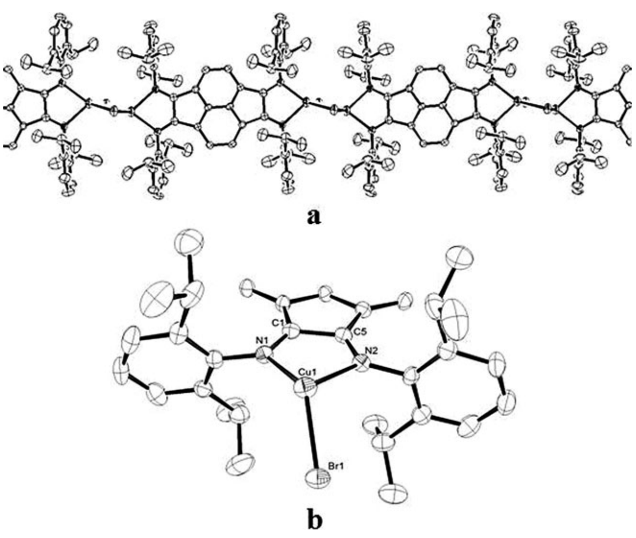

Fig. 1 (a) ORTEP view of polymer **5**, with thermal ellipsoids shown at 50% probability. (b) View of a fragment of the monomeric unit of **5**. Selected bond lengths (Å) and angles (°): C(1)–C(5) 1.504(8), C(1)–N(1) 1.276(7), C(5)–N(2) 1.274(7), N(1)–Cu(1) 2.099(4), N(2)–Cu(1) 2.116(4), Cu(1)–Br(1) 2.4132(11); N(1)–C(1)–C(5) 118.6(5), C(1)–C(5)–N(2) 118.5(5), C(1)–N(1)–Cu(1) 110.4(4), C(5)–N(2)–Cu(1) 110.0(4), N(1)–Cu(1)–N(2) 80.52(16). Each Cu_2Br_2 moiety is located on an inversion center, and the asymmetric unit features half of the ligand, which lies about another inversion center.

sum of their covalent radii, hence there is no evidence of a bonding interaction between these atoms.

Treatment of one equivalent of **2** with four equivalents of BCl_3 in a CH_2Cl_2/hexanes solution at 25 °C for 12 h resulted, after work-up of the reaction mixture, in a virtually quantitative yield of the boron dication salt $[Cl_2B(dpp\text{-}TIP)BCl_2][BCl_4]_2$ (**6**). Compound **6** was characterized on the basis of spectroscopic measurements[3] and an X-ray diffraction study.[4] Although the accuracy of the structure is not high due to crystal twinning, the data were adequate to establish the atom connectivity (Fig. 2) and approximate bond orders. For example, the N–C (av. 1.281(9) Å) and C–C (av. 1.501(10)) distances correspond to bond orders of 2 and 1, respectively; thus indicating that both of the diimine functionalities form donor–acceptor bonds to a $[BCl_2]^+$ moiety. Both BN_2C_2 rings are essentially planar, as in the case of BIAN-supported $[BCl_2]^+$ cations.[5]

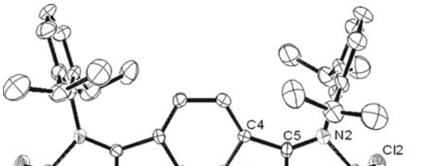

Fig. 2 ORTEP view of diboron dication **6**, with thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): C(1)–C(5) 1.501(1), C(1)–N(1) 1.285(9), C(5)–N(2) 1.278(9), N(1)–B(1) 1.634(11), N(2)–B(1) 1.625(10), B(1)–Cl(1) 1.784(9), B(1)–Cl(2) 1.786(8); N(1)–C(1)–C(2) 111.5(6), C(1)–C(2)–N(2) 111.9(6), C(1)–N(1)–B(1) 109.3(6), C(2)–N(2)–B(1) 109.6(6), N(1)–B(1)–N(2) 97.4(5), Cl(1)–B(1)–Cl(2) 113.3(5). Molecules of **6** are located on an inversion center.

We are grateful to the Robert A. Welch Foundation (F-0003) for their financial support of this work.

Notes and references

1 See, for example: (*a*) R. van Asselt, E. E. C. G. Gielens, R. E. Rulke and C. J. Elsevier, *J. Chem. Soc., Chem. Commun.*, 1993, 1203; (*b*) R. van Asselt, K. Vrieze and C. J. Elsevier, *J. Organomet. Chem.*, 1994, **480**, 27; (*c*) R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek and R. Benedix, *Recl. Trav. Chim. Pays-Bas*, 1994, **113**, 88; (*d*) B. S. Williams, P. M. Leatherman, D. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2005, **127**, 5132; (*e*) A. M. Kluwer, T. S. Koblenz, T. Jonischkeit, K. Woelk and C. J. Elsevier, *J. Am. Chem. Soc.*, 2005, **127**, 15470; (*f*) J. M. Rose, A. E. Cherian and G. W. Coates, *J. Am. Chem. Soc.*, 2006, **128**, 4186.

2 M. D. Clayton, Z. Marcinow and P. W. Rabideau, *Tetrahedron Lett.*, 1998, **39**, 9127.

3 *Spectroscopic data for* **2**: ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (d, 24H), 1.17 (d, 24H), 2.89 (sept, 8H), 6.44 (d, 4H), 7.22 (br, m, 12H). HRMS (CI^+, CH_4): calc. for $C_{62}H_{72}N_4$: 873.5835; found: 873.5833. *Spectroscopic data for* **3**: ^1H NMR (300 MHz, CD_2Cl_2): δ 0.78 (d, 24H), 1.32 (d, 24H), 3.17 (sept, 8H), 6.59 (d, 4H), 7.39 (br, m, 12H). HRMS (CI^+, CH_4): calc. for $C_{72}H_{62}Cl_4N_4Zn_2$: 1140.3094; found: 1140.3109. *Spectroscopic data for* **4**: ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 24H), 2.33 (s, 12H), 6.62 (d, 4H), 6.93 (s, 8H). HRMS (CI^+, CH_4): calc. for $C_{50}H_{48}N_4$: 704.3957; found: 704.3953. *Spectroscopic data for* **5**: ^1H NMR (300 MHz, CD_3CN): δ 0.83 (br, s, 24H), 1.24 (br, s, 24H), 3.08 (br, s, 8H), 6.41 (br, s, 4H), 7.37 (br, s, 12H). HRMS (CI^+, CH_4): calc. for $C_{62}H_{72}Br_2Cu_2N_4$: 1156.2716; found: 1156.2726. *Spectroscopic data for* **6**: ^1H NMR (300 MHz, CD_2Cl_2): δ 0.93 (d, 24H), 1.33 (d, 24H), 3.15 (sept, 8H), 6.83 (d, 4H), 7.44 (br, m, 12H).

4 All X-ray data sets were collected at 153 K on a Nonius-Kappa CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). *Crystal data for* **2**·$CHCl_3$: $C_{64}H_{74}Cl_6N_4$, monoclinic, space group $P2_1/n$, a = 12.673(3), b = 15.048(3), c = 18.514(4) Å, β = 97.68(3)°, V = 3499.1(12) Å^3, Z = 2, ρ_{calc} = 1.055 g cm^{-3}, $2\theta_{max}$ = 54.88, total reflections collected = 13 524, unique reflections = 7960 (R_{int} = 0.0419), μ = 0.282 mm^{-1}, final R indices: R_1 = 0.0692, wR_2 = 0.2071, GOF = 1.002. *Crystal data for* **3**·6$CHCl_3$: $C_{68}H_{78}Cl_{22}N_4Zn_2$, triclinic, space group P-1, a = 13.151(5), b = 15.312(5), c = 23.978(5) Å, α = 81.542(5), β = 77.600(5), γ = 64.858(5)°, V = 4260(2) Å^3, Z = 2, ρ_{calc} = 1.451 g cm^{-3}, $2\theta_{max}$ = 54.92°, total reflections collected = 28 557, unique reflections = 19 305 (R_{int} = 0.0398), μ = 1.293 mm^{-1}, final R indices: R_1 = 0.0732, wR_2 = 0.1824, GOF = 1.048. *Crystal data for* **4**·CH_2Cl_2: $C_{51}H_{50}Cl_2N_4$, monoclinic, space group $P2_1/c$, a = 13.568(3), b = 24.864(5), c = 13.852(3) Å, β = 111.16(3)°, V = 4357.6(15) Å^3, Z = 4, ρ_{calc} = 1.204 g cm^{-3}, $2\theta_{max}$ = 54.92°, total reflections collected = 28 050, unique reflections = 9946 (R_{int} = 0.0552), μ = 0.188 mm^{-1}, final R indices: R_1 = 0.0558, wR_2 = 0.01519, GOF = 1.018. *Crystal data for* **5**·THF: $C_{35}H_{44}BrCuN_2O$, monoclinic, space group $P2_1/c$, a = 13.719(3), b = 13.400(3), c = 19.628(4) Å, β = 106.77(3)°, V = 3454.9(12) Å^3, Z = 4, ρ_{calc} = 1.254 g cm^{-3}, $2\theta_{max}$ = 54.82°, total reflections collected = 22 151, unique reflections = 7850 (R_{int} = 0.0683), μ = 1.816 mm^{-1}, final R indices: R_1 = 0.0678, wR_2 = 0.02037, GOF = 1.068. *Crystal data for* **6**: $C_{58}H_{68}B_4Cl_2N_4$, monoclinic, space group $P2_1/n$, a = 16.075(3), b = 16.312(3), c = 17.424(4) Å, β = 106.66(3)°, V = 4377.2(15) Å^3, Z = 3, ρ_{calc} = 1.468 g cm^{-3}, $2\theta_{max}$ = 54.24°, total reflections collected = 5504, unique reflections = 5504 (R_{int} = 0.0525), μ = 0.613 mm^{-1}, final R indices: R_1 = 0.1189, wR_2 = 0.3692, GOF = 0.999†.

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