

Tetrakis(imino)pyracene Complexes Exhibiting Multielectron Redox Processes

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S Supporting Information

ABSTRACT: The differences in redox behavior of the monofunctional bis(imino)acenaphthene (BIAN) and bifunctional tetrakis(imino)pyracene (TIP) ligands have been explored by treatment of the latter with PI_3 , TeI_4 , or BI_3 . These reactions result in the formation of products involving the transfer of three or four electrons. Accompanying DFT calculations reveal that in each case the extent of electron transfer from each p-block element into the TIP ligand is dependent upon the element–TIP bonding interactions.

Recently, the tetrakis(imino)pyracene (TIP) ligand was developed as a bifunctional analog of the bis(imino)acenaphthene (BIAN) ligand class.¹ Subsequently, it was demonstrated that TIP ligands are capable of undergoing single-electron reduction at both diimine functionalities when treated with 2 equiv of the one-electron reductants K, $GeCl_2$ -dioxane, or $EuCp^*_2$ -OEt₂, resulting in a pairing of electrons over the pyracene backbone.² Given that BIAN ligands are capable of accepting up to four electrons,³ we were curious to discover whether TIP ligands are capable of undergoing further reduction.

Since it had been established previously that the monofunctional 2,6-diisopropylphenyl-substituted (dpp) BIAN ligand undergoes two-electron reduction with PI_3 to afford the phosphonium cation $[(BIAN)PI]^+$ as its $[I_3]^-$ salt,⁴ we decided to explore the corresponding reaction of the bifunctional dpp-substituted TIP ligand with 2 equiv of PI_3 . After the green-brown dichloromethane solution was stirred overnight, the crude solid was isolated, dissolved in a 9:1 dichloromethane/hexanes solution, and stored at $-15\text{ }^\circ\text{C}$ for several days, thereby affording a crop of dark red crystals of **1**. The ³¹P NMR chemical shift of δ 237.7 for the product implied that it represented the first example of a bis(phosphonium) cation and inferentially that four-electron reduction had occurred. Confirmation of this view was provided by a single-crystal X-ray diffraction study of **1** (Figure 1). Noteworthy structural changes that take place upon ligation to the P⁺ centers include shortening of the C(1)–C(5) distance from 1.549(4) Å in the uncoordinated TIP ligand to 1.392(8) Å in **1** and elongation of the average C–N bond distance from 1.268(3) Å to 1.350(7) Å.

The corresponding reaction of the TIP ligand with 2 equiv of TeI_4 resulted in the isolation of a blue-green solid following

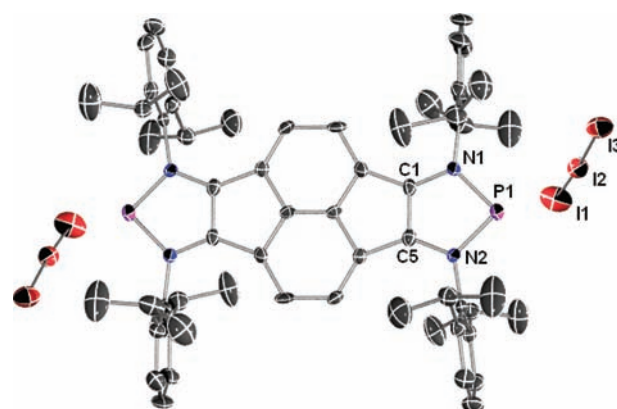


Figure 1. POV-Ray view of **1** with thermal ellipsoids shown at 40% probability. All hydrogen atoms and two molecules of lattice CH_2Cl_2 have been removed for clarity.

solvent removal. After washing the crude solid with hexanes to remove the residual iodine, crystals of **2** were obtained by storage of a 4:1 dichloromethane/hexanes solution at $-15\text{ }^\circ\text{C}$ for several days. The reaction of TeI_4 with tetrakis(imino)pyracene also involves a four-electron reduction. However, contrary to the ligand-based reduction that occurred in the case of **1**, the reduction takes place at the Te centers to afford the bis(TeI_2) complex **2**. No reduction of the TIP ligand occurred as evidenced by the X-ray crystal structure (Figure 2) which revealed the presence of a C(1)–C(5) single bond and two C=N double bonds within each of the C_2N_2Te rings. It has been elegantly demonstrated by Ragona et al. that the analogous (TeI_2)BIAN compound can serve as a synthon for a novel Te(II) dication upon halide abstraction with $Ag(OTf)$.⁵ Current efforts are ongoing to determine whether a similar synthetic pathway is accessible for **2**.

In general, the formation of these p-block derivatives involves the interplay of several factors, namely the strengths of the σ and π E–N (E = P, Te) bonding interactions, the ability of the TIP ligand to accept and delocalize electron density, the dissociation of E–I bonds with the consequent formation of I_2 and/or I^- , and the lattice energies in the case of the charged species. The first two types of contributions were examined by means of electronic structure calculations (DFT) in order to

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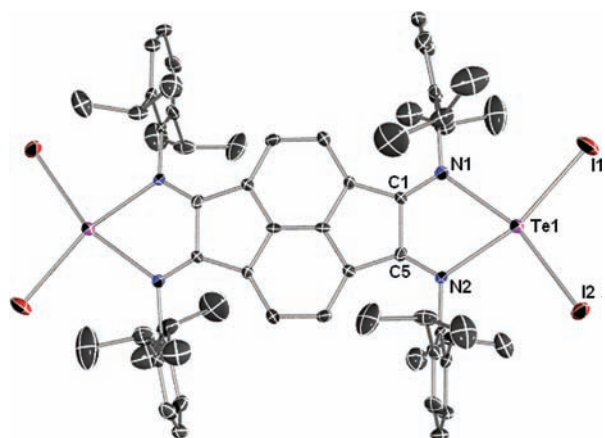


Figure 2. POV-Ray view of **2** with thermal ellipsoids shown at 40% probability. Two molecules of lattice CH_2Cl_2 and all hydrogen atoms have been removed for clarity.

interpret the observed differences in the redox behavior of **1** and **2**. Geometry optimizations, which were carried out under the general gradient approximation with the PW91 functional, provided an excellent reproduction of the molecular dimensions. The calculated electron density was then analyzed on the basis of computed Nalewajski–Mrozek bond indices (orders)⁶ and electron localization functions (ELFs).⁷ Relevant sections of the calculated ELFs are presented in Figures 3 and 4, and pertinent bond indices are compiled in Table 1.

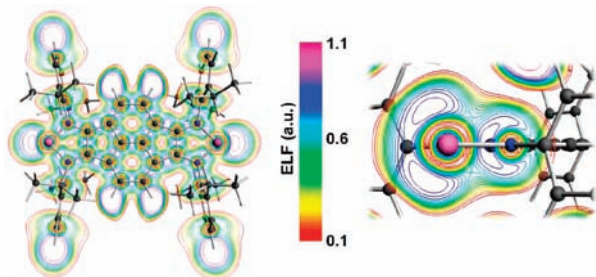


Figure 3. Contour plots of the ELF of **1** in the TIP plane and a perpendicular plane containing the P–N bond.

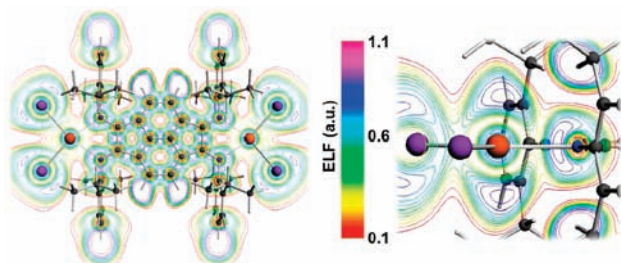


Figure 4. Contour plots of the ELF of **2** in the TIP plane and a perpendicular plane containing the Te–N bond.

The ELF contour plots in the TIP plane provide a map of the localization of the σ bonding electron pairs. In this respect, there is a significant difference between the molecules of **1** and **2**. The positions of the ELF maxima along the E–N internuclear axes indicate that the Te–N bond is considerably more polarized than the corresponding P–N bond. The weaker bonding interaction of **2** also results in the formation of more localized π electron pairs along the Te–N bonds and less

Table 1. Calculated Nalewajski–Mrozek Bond Indices around the $\text{C}_2\text{N}_2\text{E}$ Chelate Ring

	1	2	3
C–C	1.30	1.05	1.24
C–N	1.35	1.68	1.27
N–E	1.19	0.40	1.14
E–X		0.93	1.32

efficient electron sharing between the π manifold of the TIP ligand and the chalcogen. Therefore, while in the case of **1** the electron acceptor ability of the ligand is manifested in changes of bond length that are consistent with a four-electron reduction, in compound **2** two lone pairs remain centered on each tellurium atom. The calculated bond orders for **1** are consistent with the multiple bond character of the P–N link and conjugation throughout the $\text{C}_2\text{N}_2\text{P}$ ring. These values are in clear contrast with the corresponding parameters calculated for **2**, namely a small Te–N bond order and localized C–C and C=N bonds.

Attention was turned next to the reactions of the TIP and BIAN ligands with BI_3 . In previously reported work, we⁸ and others⁹ have shown that the reactions of the lighter boron trihalides BCl_3 and BBr_3 with the TIP or BIAN ligands result in straightforward heterolytic cleavage of a B–Cl or B–Br bond and formation of the anticipated boron halide salts. No evidence was found for redox behavior in any of these reactions. In sharp contrast, the reaction of the TIP ligand with BI_3 in dichloromethane solution affords the novel radical cation salt **3** (Figure 5) by transfer of three electrons into the TIP ligand.

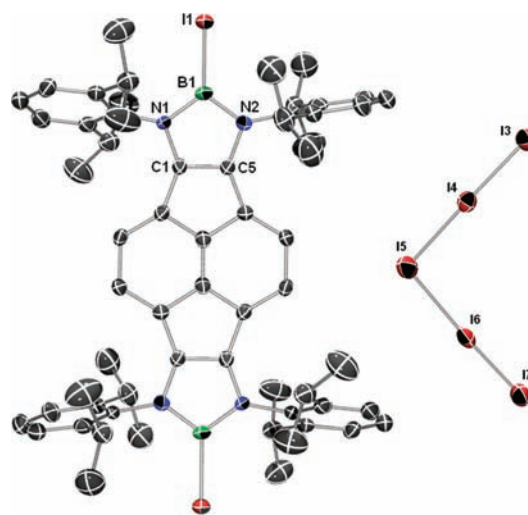


Figure 5. POV-Ray view of **3** with thermal ellipsoids shown at 40% probability. Three molecules of lattice CH_2Cl_2 and all hydrogen atoms have been removed for clarity.

Ligation of the “BI” fragments results in ligand reduction as evidenced by a shortening of the average C(1)–C(5) bond length to 1.399(7) Å and extension of the average C–N bond distance to 1.372(6) Å. A fourth electron is associated with an iodide anion which, in turn, binds to two I_2 molecules to form the pentaiodide counterion.

Unfortunately, it was not possible to record a satisfactory ESR spectrum for compound **3**. However, the observed magnetic moment of 1.74 μ_B is consistent with the presence of one unpaired electron. Unrestricted DFT calculations

indicate that the spin density (Figure 6) is concentrated on atoms B1, C1, and C5. As before, bond-order calculations were

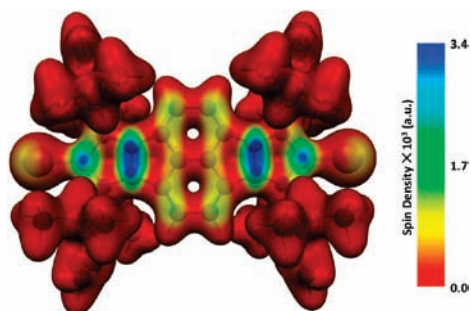


Figure 6. Projection of the spin density of **3** on the 0.03 au isosurface of the electron density.

employed to examine the bonding in **3**, the results of which are consistent with strong σ bonding interactions and efficient delocalization of π electron density onto the ligand.

Given the unanticipated course of the reaction of the TIP ligand with BI_3 , we were curious to discover the outcome of the reaction of the analogous monofunctional dpp-BIAN ligand with this boron trihalide. Accordingly, dpp-BIAN was treated with 1 equiv of BI_3 in dichloromethane solution which resulted, after workup, in the isolation of dark red, solid **4**. Recrystallization of the crude material was effected by slow evaporation of a THF solution of **4**. X-ray crystallographic analysis of **4** revealed that it is a neutral complex in which the BIAN ligand is coordinated to a BI moiety (Figure 7). Scrutiny

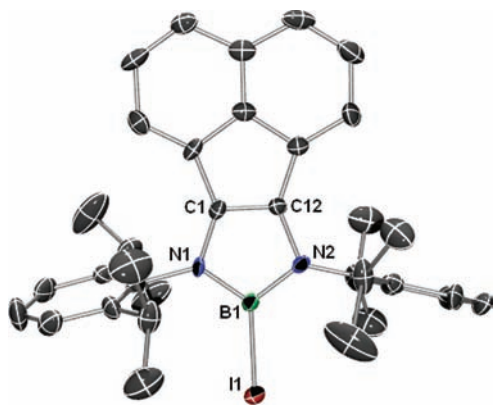


Figure 7. POV-Ray view of **4** with thermal ellipsoids shown at 40% probability. All hydrogen atoms and one molecule of lattice CH_2Cl_2 have been removed for clarity.

of the metrical parameters leads to the conclusion that two-electron reduction has taken place. Diagnostic in this regard are the C(1)–C(12) and average C–N bond distances of 1.354(6) and 1.409(6) Å, respectively. A similar conclusion has been reached by Nozaki et al. on the basis of the metrical parameters for the corresponding diazabutadiene complex, (DAB)BI.¹⁰

In conclusion, three novel TIP-supported main group complexes have been prepared that feature three- and four-electron redox events. To the best of our knowledge, compounds **1** and **3** represent the first crystallographically characterized examples of ligands that involve reduction by more than two electrons from p-block sources. In complexes **1** and **3**, the TIP ligand serves as the electron acceptor while, in

the case of **2**, reduction occurs at the Te centers. The preparation of the (BIAN)BI complex **4**, which displays a doubly reduced ligand architecture, provides further evidence that the TIP ligand class possesses a unique electronic behavior and range of reactivities in comparison with those of the monofunctional BIAN ligand.

■ ASSOCIATED CONTENT

📄 Supporting Information

Full experimental data, spectroscopic characterization, and crystallographic data are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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