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Conjugated Ligands

Naphthalene-Mediated Electronic Communication in Tetrakis(imino)pyracene Complexes**

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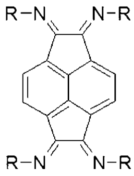
Previous work with monofunctional bis(imino)acenaphthene (bian) ligands demonstrated that they are capable of accepting zero, one, or two electrons from lanthanide bis(cyclopentadienides) depending on the choice of the metal and the steric/electronic characteristics of the bian ligand substituents.[1] More recently, the first example of a bifunctional analogue of the bian ligand class has been reported, namely the tetrakis(imino)pyracene (tip) ligand **1a** (Scheme 1).[2] The same preparative method has now afforded **1b**, an additional member of this ligand class. Herein we report the interesting redox behavior of this new type of bridging ligand. While several redox-active bridging ligands with a variety of architectures are known,[3] to the best of our knowledge their electronic and steric properties cannot be readily tuned. However, molecules with tunable electronic interactions between redox-active centers are of interest because they offer the possibility of extended delocalization of electron density.[4] Apart from being intrinsically interesting, the mediation of electronic coupling in redox-active bridging ligands is pertinent to the design of molecular electronic devices and the understanding of biochemical processes.[5]

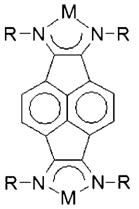


1a: R = 2,6-diisopropylphenyl (dipp)

1b: R = *p*-fluorophenyl (*p*-F)

Scheme 1. Tetrakis(imino)pyracene (tip) ligands.

Treatment of **1a** with two equivalents of potassium metal in THF solution for 12 h at ambient temperature resulted in the reaction mixture changing color from orange to green. Recrystallization of the resulting solid from THF at −15 °C afforded dark green crystals of the dipotassium complex $[(thf)_3K(dipp\text{-}tip)K(thf)_3]$ (**2**; Scheme 2).



2: M = $K(thf)_3$; R = dipp

4: M - GeCl; R = dipp

5: M = $Eu(Cp^*)_2$; R = *p*-F

Scheme 2. $[M_2(tip)]$ complexes that undergo two-electron reductions.

A single-crystal X-ray diffraction study of **2**[6] (Figure 1) revealed the coordination of a $\{K(thf)_3\}$ moiety to both ends of the tip ligand. The metrical parameters for the KN_2C_2 rings, which are symmetry-related, are consistent with the view that single-electron transfer had taken place at both diimine functionalities. Specifically, the C−C and C−N bond lengths of 1.484(5) and 1.320(6) (av) Å, respectively, for the KN_2C_2 rings fall between those of typical single and double bonds. Confirmation of this assignment was provided by the synthesis and structural analysis of the corresponding monoanionic complex [K(dipp-bian)] (**3**), for which the C−C and C−N (av) bond lengths are 1.448(4) and 1.317(4) Å, respectively. The potassium ions of **2** are located on opposite sides of the tip ligand and the distance between the K^+ centers is 12.61 Å. However, a slight deviation from overall skeletal planarity is evidenced by the modest angle of 7.63(3)° between the N-C-C-N and N-K-N planes. The average N−K and K−O(thf) distances are 2.703(3) and 2.768(2) Å, respectively. Interestingly, **2** is diamagnetic, thus implying that the two otherwise unpaired electrons in the C_2N_2K rings occupy

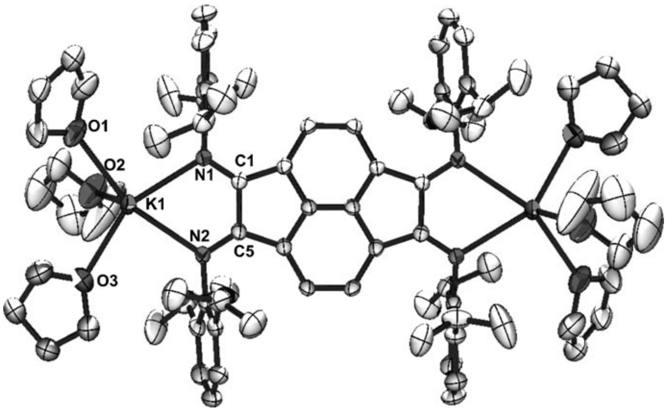


Figure 1. POV-RAY diagram for **2** shown with thermal ellipsoids at 50% probability. All hydrogen atoms have been omitted for clarity.

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Supporting information for this article (Experimental details for the synthesis and characterization of the new ligand **1b** and complexes **2**–**6** along with the details of the DFT/B3LYP calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.200904122.

the lowest unoccupied molecular orbital (LUMO) of the dipp-tip ligand.

To gain inisight into the electronic structure of **2**, the products of the sequential addition of four electrons to the model H_4tip ligand were explored under idealized D_{2h} symmetry by means of DFT/B3LYP calculations.[7] The addition of two electrons resulted in a lengthening of the C−N bonds from 1.2750 to 1.3294 Å, shortening of the C−C bonds in the diimine moieties from 1.5480 to 1.5040 Å, and contraction of the central C−C bond of the naphthalene unit from 1.3760 to 1.3400 Å. The corresponding C−N and C−C bond lengths for the H_4tip dianion are close to those cited earlier for the X-ray structure of **2**, as is the experimental bond length of the central C−C bond of the naphthalene moiety (1.352(3) Å). The DFT/B3LYP calculations on the H_4tip ligand also provided valuable insight into the mode of the interaction between the unpaired electrons of **2.** The composition of the LUMO of H_4tip ($4b_{1u}$; Figure 2) can be traced back to the in-phase combination of the LUMOs of the two N-C-C-N fragments. Such strong orbital interaction is mediated by the π orbitals of the naphthalene rings. The overall result is that the two highest energy electrons of the dianion are effectively paired in an orbital which is delocalized over both diazabutadiene moieties and the naphthalene bridge, and possesses N−C antibonding and C−C bonding character. The enhanced delocalization results in the two-electron reduction having a smaller effect on the bond lengths of the H_4tip ligand than on those of the corresponding monofunctional H_2bian ligand. The spin pairing can also be understood on the basis of the pair of resonance structures displayed in Scheme 3.[8] The overall electronic structure arises from equal weighting of these two canonical forms.

The structure of **2** itself was also investigated at the same level of theory and found to exhibit all the salient features of the single-crystal X-ray structure. In particular, the N−K (2.7373 Å) and K−O(thf) (2.7443 Å) separations were reproduced accurately, and the C−C (1.4845 Å) and C−N (1.3292 Å) bond lengths within the diazabutadiene fragments were found to be very similar to those computed for the H_4tip dianion. The contraction of the central C−C bond of the naphthalene fragment was also modeled satisfactorily (0.021 Å).

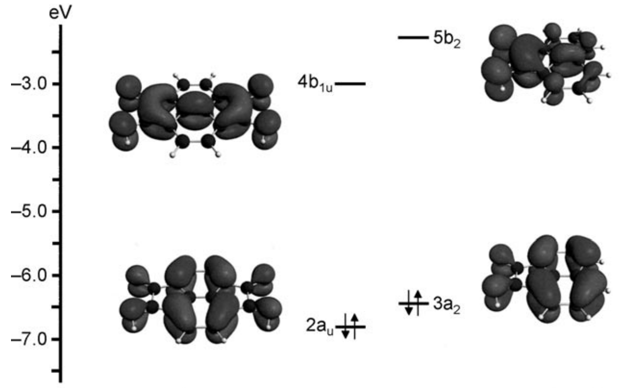
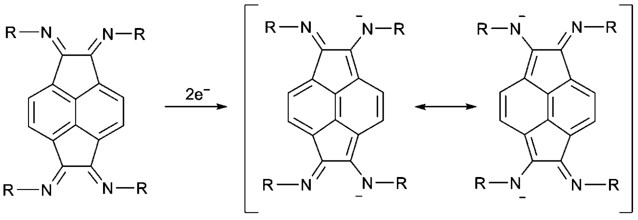


Figure 2. H_4tip and H_2bian frontier orbitals calculated using B3LYP.



Scheme 3. Resonance forms for the doubly reduced tip ligand.

The reaction of four equivalents of $[GeCl_2(1,4\text{-dioxane})]$ with one equivalent of the dipp-tip ligand **1a** resulted, after workup, in a virtually quantitative yield of the green bis(chlorogermyl) compound **4**, the structure of which is illustrated in Figure 3. Akin to **2**, compound **4** is diamagnetic, and the C(1)−C(5) and average C−N bond lengths of 1.452(7) and 1.322(6) Å, respectively, are comparable with those of **2**. The other product of this reaction is Ge_2Cl_6. The analogous monogermanium complex [GeCl(dipp-bian)] has been reported by Fedushkin et al.,[9] and was shown to possess a radical anion structure in which the unpaired electron is located primarily on the N-C-C-N moiety.[10]

An analogous result was obtained when decamethyleuropocene was employed as a one-electron reductant in the complex $[(Cp^*)_2Eu(p\text{-F-tip})Eu(Cp^*)_2]$ ($Cp^* = C_5Me_5$) (**5**). In this case, it was necessary to use *p*-fluorphenyl substituents on the tip ligand, to decrease the steric interactions at the coordination sites and to facilitate electron transfer from the Eu^{2+} center to the tip ligand.[11] As in the case of **2**, single-electron transfer from both metal sites was evident from the C−C and C−N bond lengths of 1.480(10) and 1.327(9) Å, respectively, which were determined by single-crystal X-ray diffraction (Figure 4).[6] Comparison of the structure with that of $[Cp^*_2Eu(p\text{-F-bian})]$ (**6**) revealed similar metrical parameters for the corresponding C−C and C−N (av) bond lengths, namely 1.453(7) and 1.339(7) Å, respectively. The skeletal structures of both **5** and **6** are distinctly nonplanar, as indicated by the angles of 17.69° and 20.81° between the N-

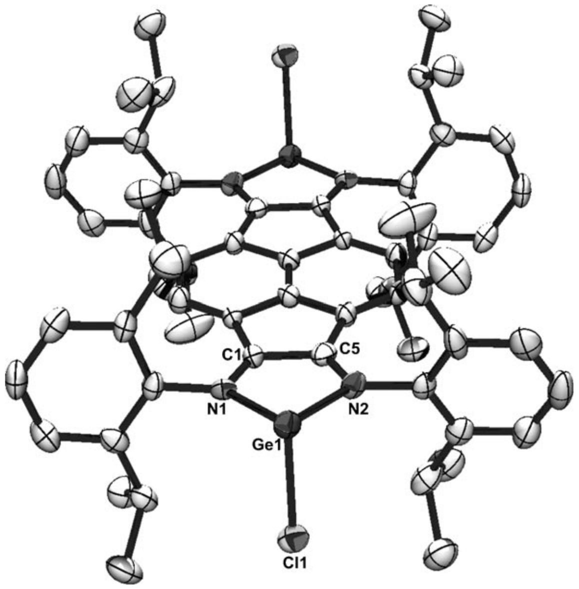


Figure 3. POV-RAY diagram for **4** shown with thermal ellipsoids at 50% probability. All hydrogen atoms have been omitted for clarity.

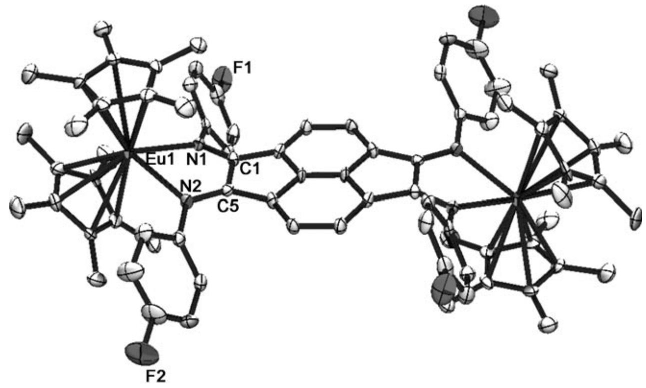


Figure 4. POV-RAY diagram for **5** with thermal ellipsoids at 50% probability. All hydrogen atoms have been omitted for clarity.

C-C-N and N-Eu-N planes, respectively. The reason for this deviation from planarity stems primarily from the minimization of the steric interactions between the *p*-fluoroaryl rings and the methyl groups of Cp*. For both complexes, the average distances of 2.450 Å between the ring centroid and the europium center are indicative of a Eu oxidation state of +3.[12] The magnetic moment value of 3.86 BM, as measured by the Evans method, is close to those of the biseuropium(III) complex [{EuF(hfac)$_3$K(diglyme)}$_2$] (3.7 BM)[13] and the monoeuropium(III) complex [Cp*$_2$Eu(*p*-F-bian)] (2.80 BM), which suggests that there is little or no interaction between the Eu^{3+} centers of **5**.

Further evidence that Eu→ligand electron transfer had taken place in complexes **5** and **6** stemmed from the absence of C=N stretching vibrations at 1620 cm^{-1} in the IR spectra and the detection of signals at $\delta = -21.9$ ppm (**5**) and -21.7 ppm (**6**), which are attributable to the Cp* groups, by ^{1}H NMR spectroscopy. These values are similar to that of $\delta = -19.7$ ppm reported for the Eu^{3+} complex [Cp*Eu(OCMe$_3$)(μ-OCMe$_3$)$_2$] by Evans et al.[14]

In summary, bifunctional terakis(imino)pyracene (tip) ligands have been shown to undergo single-electron reduction at both diimine functionalities when treated with potassium metal, germanium dichloride dioxanate, or decamethyleuropocene. The transferred electrons pair up in an orbital that is delocalized over both diazabutadiene moieties and the naphthalene bridge and possesses N−C antibonding and C−C bonding character. Future work will focus on electronic communication mediated by larger aromatic systems.

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Keywords: bifunctional ligands · density functional calculations · electronic communication · ligand effects · redox chemistry

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[6] Crystallographic data for **2**: $C_{86}H_{120}K_2N_4O_6$, $M_r = 1384.06$, $T = 153(2)$ K, monoclinic, space group $P2_1/n$, $a = 13.581(5)$, $b = 17.668(5)$, $c = 18.964(5)$ Å, $\beta = 107.043(5)°$, $V = 4351(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.057$ Mg m^{-3}, $\mu = 0.158$ mm^{-1}, 16516 reflections collected, 9963 independent reflections ($R_{int} = 0.0435$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0821$, $wR_2 = 0.2351$. **3**: $C_{36}H_{40}KN_2$, $M_r = 539.80$, $T = 153(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.368(3)$, $b = 24.327(5)$, $c = 12.812(3)$ Å, $\beta = 109.32(3)°$, $V = 3637.7(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.986$ Mg m^{-3}, $\mu = 0.168$ mm^{-1}, 12892 reflections collected, 6902 independent reflections ($R_{int} = 0.0660$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0715$, $wR_2 = 0.1790$. **4**: $C_{76}H_{88}Cl_2Ge_2N_4$, $M_r = 1273.58$, $T = 153(2)$ K, monoclinic, space group $P2_1/n$, $a = 11.689(2)$, $b = 17.192(3)$, $c = 19.130(4)$ Å, $\beta = 107.54(3)°$, $V = 3665.8(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.154$ Mg m^{-3}, $\mu = 0.934$ mm^{-1}, 11704 reflections collected, 6452 independent reflections ($R_{int} = 0.1087$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0713$, $wR_2 = 0.1820$. **5**: $C_{106}H_{112}Eu_2F_4N_4$, $M_r = 1821.92$, $T = 153(2)$ K, triclinic, space group $P\bar{1}$, $a = 13.648(3)$, $b = 13.792(3)$, $c = 14.410(3)$ Å, $\alpha = 82.45(3)°$, $\beta = 66.98(3)°$, $\gamma = 70.30(3)°$, $V = 2350.5(8)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.287$ Mg m^{-3}, $\mu = 1.377$ mm^{-1}, 15893 reflections collected, 10647 independent reflections ($R_{int} = 0.0596$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0782$, $wR_2 = 0.1835$. **6**: $C_{44}H_{44}EuF_2N_2$, $M_r = 790.77$, $T = 153(2)$ K, monoclinic, space group Cc, $a = 21.972(5)$, $b = 10.238(5)$, $c = 18.282(5)$ Å, $\beta = 119.046(5)°$, $V = 3595(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.461$ Mg m^{-3}, $\mu = 1.789$ mm^{-1}, 11969 reflections collected, 7709 independent reflections ($R_{int} = 0.0297$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0370$, $wR_2 = 0.0807$. CCDC 732618 (**1b**), 732617 (**2**), 732620 (**3**), 739106 (**4**), 732619 (**5**), and 732616 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] See the Supporting Information for details.

[8] We are grateful to a referee for this suggestion.

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[10] For a recent review of related bian-supported main-group complexes, see N. J. Hill, I. Vargas-Baca, A. H. Cowley, *Dalton Trans.* **2009**, 240–253.

[11] Cyclic voltammetry measurements indicate that the first two reductions of ligand **1a** occur at −1.12 and −1.68 V, while those of ligand **1b** occur at −0.83 and −1.22 V.[7]

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