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COMMUNICATION

Classifying donor strengths of dipyrrinato/aza-dipyrrinato ligands

Roberto M. Diaz-Rodriguez,[a] Katherine N. Robertson[b] and Alison Thompson*[a]

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A parameter is reported by which to use ^{13}C NMR chemical shifts to measure and predict the donor capabilities of N^N dipyrrinato and aza-dipyrrinato ligands chelating in L^X fashion. The results enable the rationalisation of the properties of these ligands and their complexes, as well as enable rational design incorporating both steric and electronic considerations when tuning to effect desired applications. Complexes containing these ligands are prevalent due to their desirable photophysical properties such as high chemical stability, resistance to photodegradation, strong absorbance, and ease of chemical modifiability.

Dipyrrins are a family of fully conjugated dipyrrolic compounds that are intensely chromophoric. They are frequently used as the basis of robust and versatile dyes and sensors courtesy of their high chemical modifiability and stability.[1, 2] Dipyrrins are typically green or orange, with some examples reaching into the red region of the spectrum.[3-5] One common modification of the dipyrrin is the replacement of the bridging methine CH unit with a nitrogen atom, yielding so-called aza-dipyrrins (Figure 1).[6] This modification alone can yield red-shift of the absorption and emission maxima of up to 100 nm, thereby considerably expanding the accessible spectral domain of the chromophoric framework. The aza-dipyrrin unit has been calculated to have a much smaller HOMO-LUMO gap than that of the *meso*-methine dipyrrin, providing rationale for the substantial red-shifts originating with differences in electron density distribution across the two frameworks.[7] There are marked differences in reactivity of the aza-dipyrrin skeleton relative to that of the *meso*-methine dipyrrin unit. For example, many *meso*-methine dipyrrins are not stable as free-bases and must be stored and used as their HX (typically HBr) salts.[2, 8] In contrast, aza-dipyrrins are almost exclusively handled as free-bases and are air-stable in that form. Furthermore, we have recently reported that sodium and potassium salts of aza-dipyrrins are synthetically useful, while the same salts of *meso*-methine dipyrrins display uncontrollable reactivity.[9, 10]

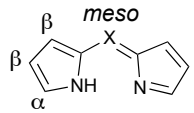

Figure 1. The (aza-)dipyrrin core and positional nomenclature.

Complexes containing dipyrrinato ligands are especially valuable. Beyond their use in biosensing, the tunable photophysical and chemical properties[1, 4, 11-13] of fluorophoric dipyrrinato boron complexes (BODIPYs) have enabled utility as photosensitizers for photodynamic therapy[5, 11, 14] and photovoltaics,[13, 15, 16] as emitters for OLEDs,[17] and as catalysts.[18-20] Fluorescent dipyrrinato metal complexes are also known,[21-24] although such complexation tends to temper the emission.

Although a plethora of dipyrrinato and aza-dipyrrinato complexes spanning the periodic table have been reported,[2, 25-27] a fundamental, empirical understanding of the electronic properties of these compounds is still incomplete, especially as it pertains to their use as ligands for metals and metalloids. Despite some comparative work between dipyrrins and aza-dipyrrins as chromophores,[7] a direct comparison of these skeletons in terms of coordination chemistry is exigent, particularly as the need for complexes that absorb and/or emit at long wavelengths grows due to potential in therapeutic,[11, 14, 28] photovoltaic,[13, 16, 29] and biological imaging[4, 5, 12, 14, 30-32] applications.

For inorganic and organometallic complexes, the electron-donating capabilities of the ligands are crucially intertwined with the overall properties of the complex. A measurement of donor strength for dipyrrins and aza-dipyrrins is missing from the literature, despite this ligand class becoming increasingly popular. The classical Tolman parameter (TEP)[33] is ineffective for this purpose, as it does not accurately predict the electronics of bidentate, L^L or L^X-type ligands such as those of interest herein. Although modern methods allow the evaluation of a wider range of ligand classes, generality is yet to be demonstrated.[34] However, the group of Huynh developed a ligand electronic parameter that is accurate, highly sensitive, extremely facile, and expandable to a variety of ligand classes.[35-37] It

[a] *Department of Chemistry, Dalhousie University, PO BOX 15000 Halifax, Nova Scotia B3H 4R2, Canada. E-mail: Alison.Thompson@dal.ca*
[b] *Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia B3H 3C3, Canada*

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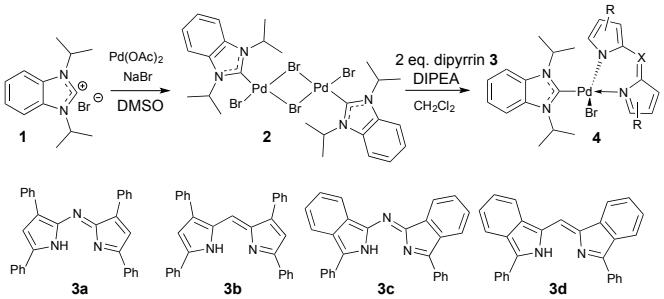
is based upon a square-planar palladium(II) complex which contains a 1,3-diisopropylbenzimidazolin-2-ylidene (iPr_2-bimy)[38] unit and the ligand to be evaluated. The value of the ^{13}C chemical shift of the carbene carbon atom in the iPr_2-bimy unit is given as the electronic parameter, termed "HEP2",[34] and is used to quantify the donor strength of the ligand *trans* to the carbene. Stronger donors push this resonance further downfield. Although the iPr_2-bimy probe used for HEP2 measurements is directly sensitive to the magnitude of the *trans*-influence, the entire chelator affects the electronics of the metal center. The HEP2 parameter for measuring the net donor strength of the chelating ligand is thus convenient and well-suited to dipyrrins. Furthermore, comparisons can be drawn with other common L^X-type ligands quantified via the same method, including diimines, biaryls such as bipyridine and phenanthroline, and dicarbene-type structures.[37] Note that HEP2 should not be confused with the similar, but distinct, HEP parameter that measures σ-donor strengths of monodentate L-type ligands.[34]

Herein we report the synthesis and characterization of complexes of the type PdBr(iPr_2-bimy)(L^X) where L^X refers to an N^N dipyrrinato or aza-dipyrrinato monanionic chelator. Synthesis of these complexes began with the treatment of benzimidazole with isopropyl bromide to generate benzimidazolium salt **1**, followed by complexation with palladium acetate and sodium bromide to yield the bromo-bridged precursor complex **2**.[38] To investigate the differences in electronic properties of dipyrrins and aza-dipyrrins, an isostructural series of four dipyrrins (**3a-d**) was chosen. Treatment of **2** with dipyrrins **3a-d** under basic conditions yielded the corresponding complexes **4a-d** (Scheme 1). This series represents the two prevailing structural supertypes of aza-dipyrrin (i.e. tetra-aryl and ring-fused)[6] and their *meso*-methine analogues.



Scheme 1. Synthesis of complexes for the measurement of ligand donor ability.

Complexes **4a-d** are non-emissive, robust against air and moisture and are easily handled without precautions. This stability is reflective of the favored d^8, LBN = 4, 16-electron, square-planar configuration adopted by the complexes. X-ray quality crystals of **4a** were grown by slow evaporation of a dichloromethane/pentane solution, and the crystal structure of this compound is shown in Figure 2.[39] The geometry around the palladium center is thus confirmed to be square planar, with an angular sum of 360.38°. Individual angles are slightly distorted owing to the relatively acute dipyrrinato bite angle of 85.41(6)°. Interestingly, the coordination plane about palladium is not coincident with the plane of the chelated dipyrrinato core; in fact, the dipyrrinato unit is canted substantially relative to the coordination plane. The planarity of the dipyrrin core itself is also disrupted somewhat by complexation.

Analysis of the NMR spectra of this complex suggests that the iPr_2-bimy ligand lacks rotational symmetry, which is supported by the crystal structure: the iPr_2-bimy ligand is locked between the large bromo ligand and the proximal phenyl group of the dipyrrin. Steric considerations also cause the bromo ligand to lie slightly above the palladium coordination plane. Such rotation-locking of iPr_2-bimy ligands is reflected in the NMR spectra of all complexes **4a-d**.

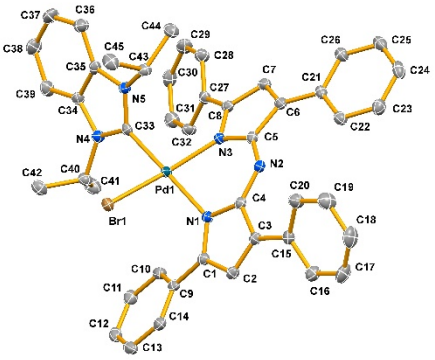


Figure 2 ORTEP diagram of **4a**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

Computational studies of BODIPYs[7] have shown that the nature of the *meso*-position contributes significantly to the energy of the LUMO, which is why the inclusion of an electronegative nitrogen atom at this position narrows the FMO gap so drastically. An electronegative atom at this position would also draw electron density away from the chelating (pyrrolic) nitrogen atoms, making an aza-dipyrrin less donating overall than its *meso*-methine analogue. Further, the electron density at nitrogen in the parent building block pyrrole is an intrinsic component of the aromatic π-system. Increasing the conjugation of the dipyrrin core (e.g. via ring-fusion) delocalizes the pyrrolic nitrogen electron density over a larger area, but also increases the amount of electron density available to the system, and the overall donicity of the resulting dipyrrinato ligand depends on the balance of these effects. The tetraphenyl *meso*-methine dipyrrin **3b** should thus be the best donor, as it would have the most electron density at the pyrrolic nitrogen atoms, and the benzannulated aza-dipyrrin **3c** should be the poorest donor as it has both extended conjugation and the electronegative *meso*-nitrogen with which to withdraw electron density from the chelating nitrogen atoms. The electronic and photophysical properties of these complexes are summarized in Table 1: the properties of the corresponding free ligands for comparison can be found in the Supplementary Information. All complexes display a red-shift and a modest increase in molar absorptivity relative to their free ligand, and the red-shifts are of similar magnitude. Determination of the HEP2 values for these complexes reveals that the ligand donor strength increases in the expected order **3c** < **3d** < **3a** < **3b**. Indeed, **3b** is the strongest donor, as it lacks both the extended conjugation and the electronegative *meso*-nitrogen.

The sensitivity of the HEP2 probe is ca. 0.1 ppm (the equivalent electronic contribution of the inductive electron-donating effect of a single methyl group).[37] The electronic similarity between tetraphenyl aza-dipyrrin **3a** and benzannulated *meso*-methine dipyrrin **3d** is reported via HEP2 values that differ by only 0.1 ppm, and essentially identical complex absorbance maxima. In comparison to **3b**, a similar reduction in donor strength is observed upon either incorporation of a *meso*-nitrogen atom or benzannulation of the dipyrrin core. If such a reduction in donicity is desired, ring-fusion of an appropriate *meso*-methine dipyrrin may serve as an alternative to the aza-dipyrrin and its accompanying synthetic challenges. If both modifications (ring fusion and the *meso*-nitrogen) are made, the donor strength is reduced in additive fashion.

To probe the general utility of this methodology and investigate the electronic properties of a variety of functionalized ligands, a second series of dipyrrins (**3e-m**, Figure 3) was bound to the PdBr(iPr$_2$-bimy) moiety to form the complexes **4e-m** following Scheme 1. The selected dipyrrins include peripheral electron-donating and -withdrawing substituents in various positions. Unfortunately, the structural scope of complexes **4** bearing aza-dipyrrinato ligands is constrained due to limitations of synthetic route to these systems. The electronic and photophysical properties of the complexes are shown in Table 1, and the properties of the corresponding free ligands can be found in the Supplementary Information.

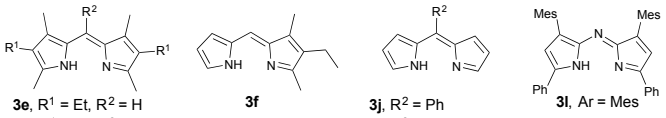
Table 1. Dipyrrins analysed via HEP2 parameter.

Table 1. Electronic and photophysical properties (in $CHCl_3$) for complexes **4a-m**.

Complex	δ carbene (ppm)	HEP2 (ppm)[a]	λ_{abs} (nm)	ε (logE)	Δ(λ_{abs}) vs. ligand[b]
4a	167.2	167.7	632	4.72	+35
4b	168.1	168.6	567	4.66	+36
4c	166.3	166.8	687	4.82	+34
4d	167.1	167.6	633	4.66	+41
4e	171.1	171.6	526 376	4.66 3.92	+77 -
4f	170.3	170.8	487 365	4.42 3.86	+91 -
4g	164.0	164.5	507 340	4.39 3.88	+45 -
4h	166.9	167.4	512	4.92	+52
4i	167.4	167.9	503	4.89	+48
4j	171.9	172.4	496	4.77	+61
4k	172.0	172.5	495 478 (sh) 360	4.70 - 4.00	+63[c] - -
4l	167.8	168.3	616	4.73	+41
4m	172.1	172.6	498 480 (sh)	4.78 -	+66

[a] HEP2 value = δ(carbene) + 0.5 ppm. [b] most bathochromic maxima. [c] compared to the free ligand value in DMSO.

Compounds **4e-m** are stable to air and moisture, and are non-emissive. The red-shifts observed upon complexation vary widely between ligands, becoming as large as 91 nm in the case of **4f**, and the magnitude of the red-shift does not follow a clearly evident trend related to electron donating/withdrawing character of substituents. X-ray quality crystals of **4h** and **4k** were analyzed, and the crystal structures are included in the Supporting Information. We were unable to obtain a crystal structure of the non-symmetric dipyrrin **4f** to verify the isomerism. The resonance of the dipyrrin core, and the nature by which dipyrrins coordinate, would make any observed donor strength difference between the two isomers small. As such, although the measurement of net donor strength of non-symmetric systems of this genre using the HEP2 method remains valid, this potential limitation is acknowledged.



3e, R^1 = Et, R^2 = H
3g, R^1 = Et, R^2 = Ph
3h, R^1 = C(O)Me, R^2 = H
3i: R^1 = CO_2Me, R^2 = H

3f

3j, R^2 = Ph
3k,R^2 = *p*-C_6H_4-OH
3m, R^2 = Mes

3l, Ar = Mes

Figure 3 Dipyrrins analysed via HEP2 parameter.

Exchange of pendant phenyl groups (as in **3b**, the strongest donor of the first series) for alkyl groups (as in **3e**, which is derived from kryptopyrrole, 3-ethyl-2,4-dimethyl-1H-pyrrole), leads to a large increase in donor strength (Figure 3 and Figure 4), evidenced by a 3 ppm downfield shift of the carbene ^{13}C resonance. Removal of some of the electron-donating substituents reduces the donor strength, as indicated by Δδ 0.2 ppm per alkyl carbon atom when comparing **3f** to **3e**. Comparison of **3e** to **3h** or **3i** reveals that exchange of a β-electron-donating substituent for an electron-withdrawing one causes a decrease in donor strength, the magnitude of which is related to the withdrawing strength of each substituent.[40] Thus, the acylated dipyrrin **3h** is a poorer donor than **3i**, and both are substantially poorer donors than the per-alkylated analogue. Furthermore, the *meso*-phenyl dipyrrin **3j** is a stronger donor than the alkylated *meso*-H dipyrrin **3e**, despite the absence of electron-donating alkyl substituents about the pyrrolic moieties. Complexes **3k** and **3m** follow suit courtesy of electron-donating hydroxyl and methyl groups, respectively. Strikingly, HEP2 tells us that the alkylated *meso*-phenyl krypto-dipyrrin **3g** is the poorest donor of all the ligands investigated here. The poor donor ability of **3g** is also evident by its reluctance to form HX salts. Whilst cognisant that the arene unit of a *meso*-aryl dipyrrin is formally cross-conjugated with the dipyrrin π-system, we were unable to find a simple rationale for the exceptionally poor donor strength of **3g** c.f. **3j** and **3m**. HEP2 indicates **3m** as a competent donor despite its larger meso-aryl unit presumably maximising cross-conjugation effects. Indeed, the constrained rotation of the *meso*-mesityl moiety within **3m** also makes this ligand the only fluorescent compound in this study.[21, 41, 42]

An investigation of aza-dipyrrinato substituent effects is useful, if limited by the requirement of extensive aryl substitution that is imparted by current synthetic methods used to access this ligand framework. Aza-dipyrrin **3l** sees exchanges of the β-phenyl substituents of **3a** for mesityl, leading to an increase in donor strength consistent with the Δδ 0.1 ppm increase expected for each methyl substituent.[37] It is clear that there is a complex interplay between substituent electronics, ligand donor strength, and photophysical properties, thus further highlighting the need for a practical measure of donicity.

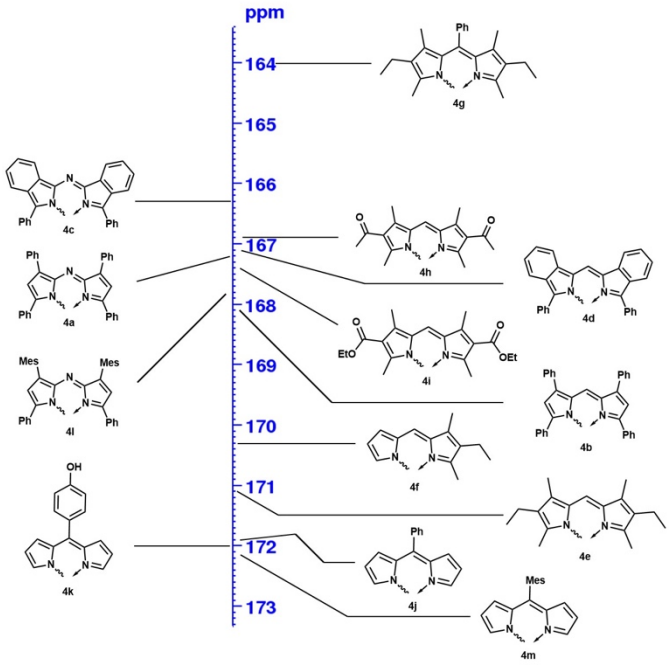


Figure 4 Carbene ^{13}C chemical shifts of the iPr_2-bimy unit of Pd-complexes **4**. More strongly donating ligands have lower-field δ values for this C atom.

The HEP2 parameter is clearly an effective measure for the donor strength of dipyrrinato and aza-dipyrrinato skeletons. Evaluating HEP2 enables an accurate comparison of these ligands to other monoanionic chelators for which this parameter is known. Varying the substituent pattern of the dipyrrinato unit allows tuning of this ligand to span a broad range of donor strengths. Figure 4 shows the ligands in order of donicity. Our values of 164 – 172 ppm place the dipyrrinato and aza-dipyrrinato ligands derived from **3a-m** as being much less electron-donating than any currently measured C^N, or carbenic, L^X-type ligand, for which values lie in the range of 180 – 200 ppm.[37] Furthermore, HEP2 indicates dipyrrinato and aza-dipyrrinato ligands as much more strongly donating than N^N type neutral chelators, e.g. bipy (162.7) or phenanthroline (161.4),[37] as expected. The dipyrrinato ligand is a borderline Lewis base, essentially σ-only and polydentate. These properties suggest that it might be a choice ligand for early transition metals and lanthanides, while also explaining its ease of complexation with softer metals like ruthenium and palladium.[2]

Conclusions

We have reported the synthesis and characterization of thirteen PdBr(iPr_2-bimy)(dipyrrinato) complexes enabling the donor capability of dipyrrins and aza-dipyrrins to be evaluated and compared for the first time. The nature of the *meso* position dominates both photophysical properties and donor strength. The presence of electron-withdrawing groups at the *beta* or *meso* positions of the pyrrolic moieties of the ligands afford marked red-shifts in their optical spectra, but also weaken their donor strength. These factors should be considered when designing (aza)-dipyrrinato ligands and complexes thereof to fulfill desired (opto)electronic properties.

Conflicts of interest

There are no conflicts to declare.

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