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SYNTHESES, STRUCTURES, AND PROPERTIES OF DIPYRIDAZINO-FUSED 1,3,4,6-TETRAAZAPENTALENES*

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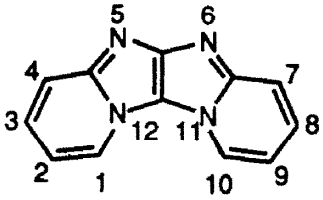
Abstract: The fluorescent 2,9-dichloro[2",3":1',2']imidazo[4',5':4,5]imidazo-[1,2-b]pyridazine (**2a**) and the unsubstituted "parent" **2b** have been synthesized. The chloro groups of **2a** were found to be easily displaced by a variety of nucleophiles to provide the 2,9-disubstituted compounds **7-12**. A single crystal X-ray structure determination of the 2,9-dimethoxy-substituted compound **7** revealed the existence of two crystallographically independent structures in the unit cell. It has been demonstrated that **2b** can form a 2:1 complex with cobalt(II).

Dipyrido[1,2-a:2',1'-f]-1,3,4,6-tetraazapentalene (**1**) is a new heterocyclic ring system that has been prepared in this Laboratory.[1-4] The main features of this compound are the 1,3,4,6-tetraazapentalene central ring array and the "bay region" formed by the four rings of the system. Replacement of the carbons at positions 1 and 10 with nitrogens would provide a "bay region" with greater electron density. Due to the lone-pair electrons of the 1,10 nitrogens, the dipyridazino[2,3-a:3',2'-f]-1,3,4,6-tetraazapentalenes **2a** and **b**[5] may act as bidentate ligands for the coordination of metals in much the same way as 1,10-phenanthroline.[6-10] Furthermore, substituents at positions 2 and 9 which have lone-pair electrons may provide additional sites for metal chelation.



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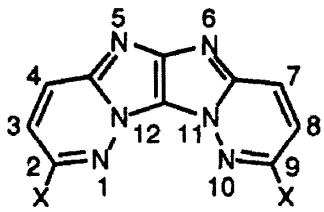

2a X=Cl
b X=H

Our initial strategy for the synthesis of **2a** and **2b** was based on the methodology (the formation of a "dimer" from two equivalents of the heterocyclic amine followed by an oxidative cyclization to produce the target compound) developed for the preparation of a number of substituted pyrido[1",2":1',2']-imidazo[4',5':4,5]imidazo[1,2-a]pyridines (**1**).[1-3] Attempts to prepare the "dimers" **5a** and **5b** (Scheme I) from two equivalents of 3-amino-6-chloropyridazine (**3a**) or 3-aminopyridazine (**3b**) and chloroketene diethyl acetal (**4**)[11,12] in an

*This article is dedicated to Edward C. Taylor, Professor of Organic Chemistry, Princeton University, on the occasion of his sixty-fifth birthday.

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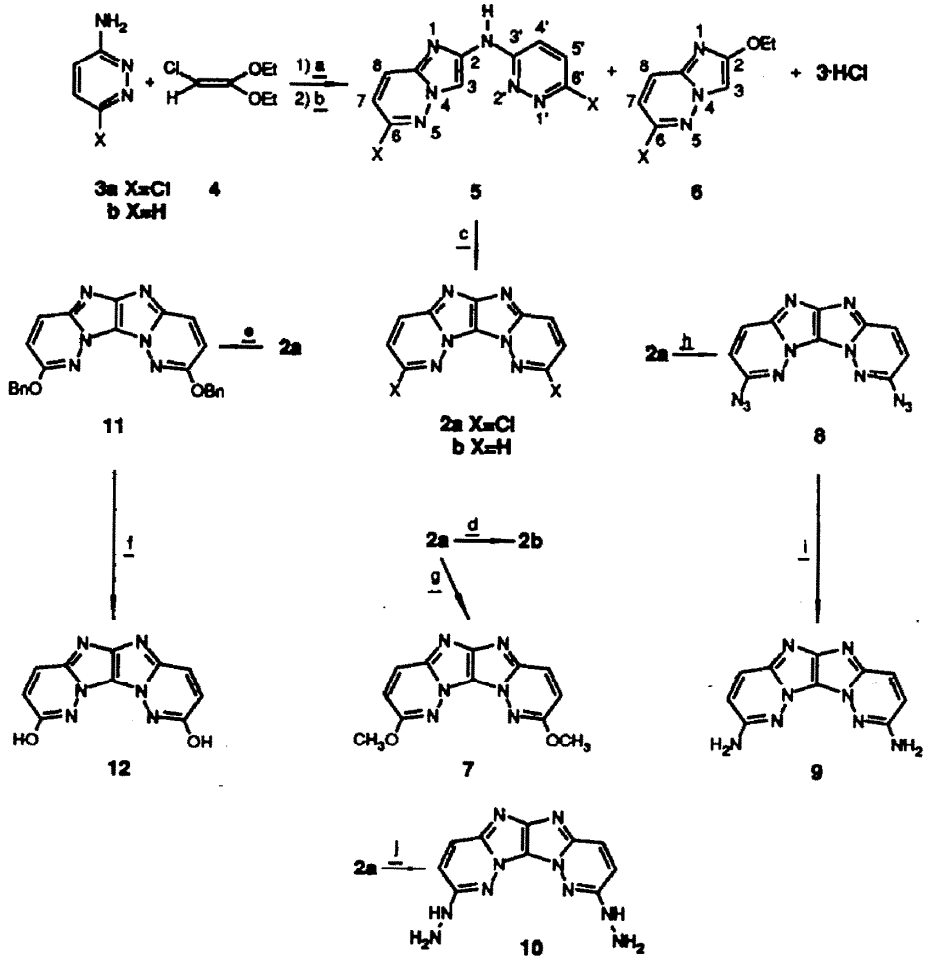
acetic acid-pyridine solution resulted in the formation of 6-chloro-3-ethoxyimidazo[1,2-b]pyridazine (**6a**) and 3-ethoxyimidazo[1,2-b]pyridazine (**6b**), respectively, as the only isolable products. However, the "dimers" **5a** and **5b** could be obtained by the treatment of **4** with one equivalent of either **3a** or **3b** in ethyl acetate to give a chloroimidate intermediate which was then allowed to react with a second equivalent of the amine (Scheme I). The course of the reaction was highly dependent upon the starting amine. The "dimerization" reaction between **3a** and **4** provided 6-chloro-*N*-(6-chloro-3-pyridazinyl)imidazo[1,2-b]-pyridazin-2-amine (**5a**) in a 50% yield (70% based on unrecovered **3a**). Also isolated from the reaction mixture was 6-chloro-2-ethoxyimidazo[1,2-b]pyridazine (**6a**) (6%) and the hydrochloride salt of **3a**. By contrast, the yield of **5b** from the reaction between **3b** and **4** was only 8%, and **6b** was isolated in a 14% yield. An unstable product that was not readily identified was also isolated from the reaction mixture.

Scheme I



a, EtOAc, 75 °C; b, **3a** or **b**, DMF, 75 °C; c, $PhI(OAc)_2$, CF_3CH_2OH; d, H_2/Pd/$CaCO_3$, DMF, methyl cellosolve; e, NaOBn, BnOH, 80 °C; f, 48% HBr, reflux; g, NaOMe, MeOH, reflux; h, NaN_3, DMF, 125-130 °C; i, H_2, Pd/C, methyl cellosolve; j, N_2H_4.

The great difference in yields between **5a** and **5b** reflect the different reactivities that are exhibited by **3a** and **3b**. Yoneda and co-workers[11] have shown that direct reaction between **3a** and phenacyl bromide gave 2-phenyl-6-chloroimidazo[1,2-b]pyridazine. Under the same conditions, **3b** gave 1-phenacyl-6-aminopyridazinium bromide, not the expected 2-phenylimidazo[1,2-b]pyridazine, by nucleophilic attack by N-2 of **3b** on phenacyl bromide. Obviously, the chloro group of **3a** has a moderating effect on the nucleophilicity of 2-aminopyridazine. By analogy, the unstable product isolated from the reaction of **3b** with **4** may have resulted from a similar nucleophilic attack by N-2 of **3b** on **4**; such an intermediate could not undergo further reaction to give **5b**.

The dipyridazino[2,3-a:3',2'-f]-1,3,4,6-tetraazapentalenes (**2a,b**) were obtained by an oxidative cyclization of **5a** or **5b** with iodobenzene diacetate[1-3] in 2,2,2-trifluoroethanol in reasonable yields (59 and 42%, respectively). The low yield of **5b** necessitated the preparation of **2b** by an alternative pathway. This was accomplished by dechlorination of **2a** by means of catalytic hydrogenation using Pd on $CaCO_3$ as the catalyst.

Since **2a** can be viewed as two fused 6-chloroimidazo[1,2-b]pyridazines that share carbons 2 and 3, we expected that **2a** would undergo nucleophilic displacement reactions similar to those observed with 6-chloroimidazo[1,2-b]pyridazine.[11,12] Generally, this was found to be true. Treatment of **2a** with sodium methoxide resulted in the displacement of both chloro groups to give **7** in 78% yield. As with 6-chloroimidazo[1,2-b]pyridazine, direct displacement of the chloro group of **2a** with liquid ammonia failed to give **9**.[12] However, the diamine **9** was obtained by the conversion of **2a** to the diazide **8** with sodium azide in DMF, followed by the reduction of the azide groups to amino groups by catalytic hydrogenation. The dihydrazino derivative **10** could be prepared in a 92% yield by treatment of **2a** with anhydrous hydrazine at room temperature.

Although the nucleophilic displacement of the chloro group of 3-substituted-6-chloroimidazo[1,2-b]pyridazines occurs at 140 °C with NaOH in EtOH,[12] **2a** failed to give the dihydroxy compound **12** under these conditions; only a diethoxy-substituted compound could be isolated. We hoped to prepare **12** by the introduction of benzyloxy groups at positions 2 and 9 followed by the removal of the benzyl groups. Compound **11** was easily prepared by the displacement of the chloro groups with sodium benzylate. Catalytic hydrogenation of **11** using Pd on carbon resulted in the disappearance of **11** from the reaction mixture (TLC); however, **12** could not be separated from the catalyst due to its extreme insolubility. Compound **12** was successfully isolated in a 64% yield by heating **11** in 48% HBr and converting the resulting hydrobromide salt into the free base. In the solid state, **12** exists in the hydroxy form, as is shown by the absence of a carbonyl stretching band in the 1750-1600 cm^{-1} region. The general insolubility of this compound precluded an examination of tautomeric forms in solution.

All of the compounds are fluorescent, although the quantum yields vary. Compounds **2b** and **7** have the highest quantum yields (0.63 and 0.69, respectively) followed by **2a** (0.33), in which heavy-atom quenching exerts its effect. Compounds **9**, **10**, and **12**, all of which are potential proton donors, have low quantum yields (0.19, 0.06, and 0.06, respectively) and exhibit two emission maxima.

Crystals of compound **7** suitable for a single crystal X-ray structure determination were obtained by the slow evaporation of a methanolic solution of **7**.

The crystals turned opaque if allowed to dry; accordingly, a crystal was mounted in a thin-walled tapered glass capillary without drying. The single crystal X-ray analysis[13] showed the presence of two crystallographically independent molecules of 7 (7a and 7b, Figure 1) and the presence of one methanol molecule for every two molecules of 7. Molecule 7a is dissymmetric about the 5a-11a bond, whereas 7b is symmetric. The bond distances in the outer rings of 7a and 7b are virtually identical and exhibit alternating single and double bond character whereas large differences exist between the bond distances of the 1,3,4,6-tetraazapentalene ring systems (rings B and C) of 7a and 7b with bonds 4a-5, 4a-12, and 5a-11a showing the greatest variance in length. The distortion from symmetry that is observed in 7a may be due to the hydrogen-bonding between N-5 and the methanol that is dispersed throughout the unit cell. Because of the disorder of the methanol molecules in the unit cell, the hydrogen-bonding pattern could not be confirmed by X-ray analysis. A similar phenomenon was observed with dipyrido[1,2-a:2',1'-f]-1,3,4,6-tetraazapentalene (1), where dissymmetry was induced by hydrogen-bonding between a molecule of water and the lone-pair electrons of the nitrogen at position 5.[2]

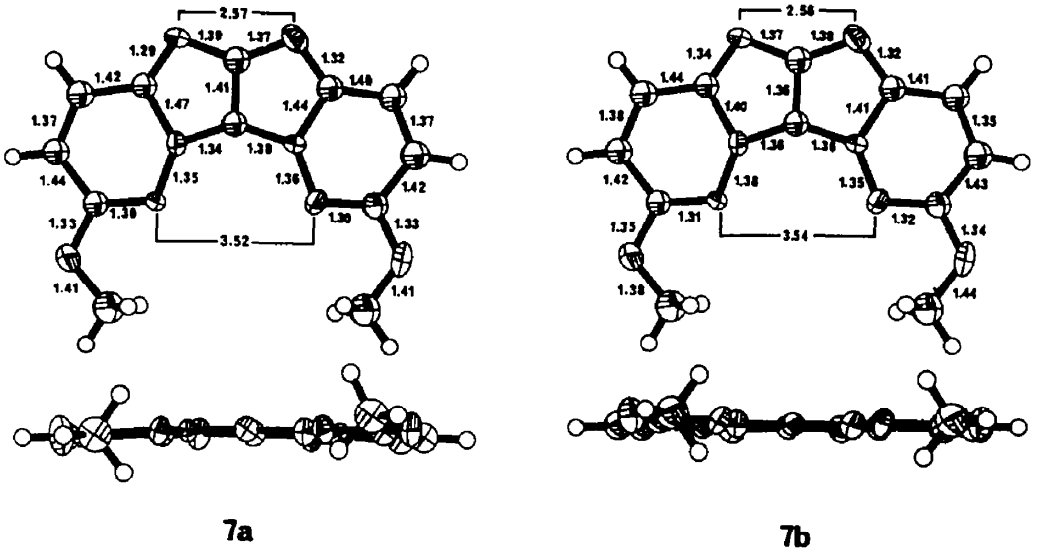


Figure 1. ORTEP drawings of the "top" and "side" view of 7 with bond lengths in angstroms as determined by X-ray analysis.

The X-ray structure analysis of 7 also revealed that both 7a and 7b are non-planar. The outer rings of 7a and 7b are virtually planar (all dihedral angles are ± 1° or ± 179°), whereas the two five-membered rings of 7a and 7b are non-planar. The dihedral angles formed by the atoms of these rings deviate from planarity by 3-9°.

Figures 2 and 3 show the ORTEP drawings and the bond lengths for 7 and 2b derived by the MMPMI[14] energy minimization program. The theoretically determined bond lengths obtained for 7 are close to those of the X-ray-determined values of the symmetrical 7b (Figure 1). The MMPMI-minimized structure of 2b has bond lengths that are virtually identical to those obtained for 7b and the energy-minimized structure of 7. The energy-minimized structure of 7 is non-planar, but in contrast to the X-ray-determined structure the two five-membered rings are planar and the two six-membered rings are non-planar. Con-

versely, the four rings of the MMPMI energy-minimized structure of **2b** are planar (all dihedral angles are 0 or 180°).

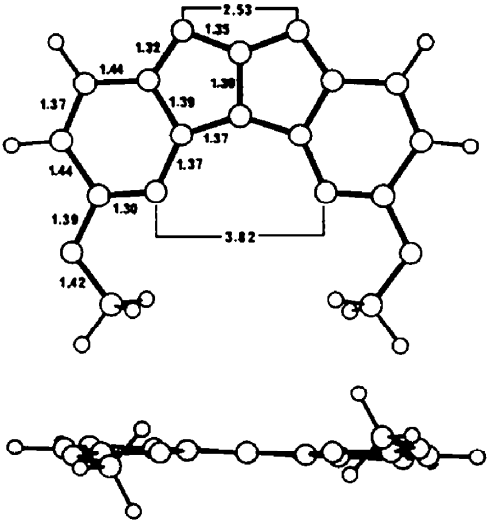


Figure 2. MMPMI-derived ORTEP drawings of the "top" and "side" view of **7**.

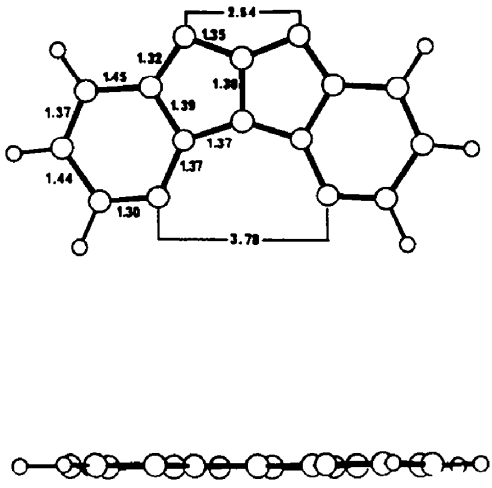
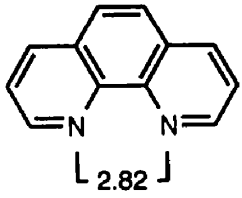


Figure 3. MMPMI-derived ORTEP drawings of the "top" and "side" view of **2b**.

The distance between the 1,10 nitrogen atoms of **7a** and **7b** is shorter (3.52 A and 3.54 A, respectively) than that predicted by MMPMI (3.82 A). This difference can be attributed to the larger value (133°) that MMPMI generates for the angle formed by atoms 1-12-11a (10-11-11a), which is 128.5° and 127.0° as determined by X-ray analysis. Therefore, the distance between nitrogen atoms 1 and 10 of **2b** derived by MMPMI is probably larger than the actual distance.



13

1,10-Phenanthroline (**13**) is an excellent bidentate ligand, due to the nitrogen atoms at positions 1 and 10, and can form either 2:1 or 3:1 complexes with Co(II), Zn(II), Fe(II), and Ru(II).[6-10] Since **2b** and **13** have similar "bay regions", **2b** would also be expected to act as a bidentate ligand. The combination of hot ethanolic solutions of **2b** and cobalt(II) chloride hexahydrate produced a blue precipitate when the starting stoichiometric ratio was either 2:1 or 3:1. Elemental microanalysis showed that the blue compound produced in either case was a 2:1 complex ([**2b**]$_2$CoCl$_2$). A 3:1 complex could not be prepared even with continued heating of the initial reaction mixture containing excess **2b**.

A further comparison of the structures of **2b** (Figure 3) and **13** reveals that the distance between the nitrogen atoms at positions 1 and 10 of **2b** is longer

than the distance between the nitrogen atoms of **13** (3.78 and 2.82, respectively). However, the distance between the nitrogen atoms at positions 5 and 6 of **2b** (2.54 Å) is only slightly shorter than the inter-nitrogen distance of **13**. Positions 5 and 6 of **2b** have a slightly greater electron density than positions 1 and 10 as predicted by a Hückel molecular orbital calculation, which raised the possibility that N-5 and N-6 might participate in the chelation of cobalt(II). For this reason, an ethanolic solution of compound **1**, in which only N-5(6) can chelate was treated with an ethanolic solution of cobalt(II) chloride hexahydrate. A blue precipitate formed immediately which by elemental microanalysis was shown to be a 2:1 complex. Therefore, we do not yet know which nitrogen atoms of **2b** are involved in the coordination of the cobalt atom. Compounds **9** and **10** also gave cobalt complexes of unknown composition under similar reaction conditions. The coordination chemistry of **1**, **2b**, **9**, and **10** is under further investigation.

EXPERIMENTAL

Instrumentation. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H Nuclear magnetic resonance (NMR) spectra (300.15 MHz) were recorded on a General Electric QE-300 Fourier-transform spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Nicolet 7199 Fourier-transform spectrophotometer. Ultraviolet/visible spectra were obtained on a Beckman Acta MVI spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Spex Fluorolog 111C spectrofluorometer coupled with a Datamate microprocessor. All excitations were conducted at 366 nm and all quantum yields are relative to the reported value of coumarin, Φ = 0.64 at λ^{ex} = 366 nm[17]. Mass spectra were obtained on a Varian MAT CH-5 instrument in the Mass Spectrometry Laboratory, School of Chemical Sciences. Elemental analyses were performed by Josef Nemeth and his staff at the University of Illinois.

6-Chloro-*N*-(6-Chloro-3-pyridazinyl)imidazo[1,2-b]pyridazin-2-amine (**5a**) and 6-Chloro-2-ethoxyimidazo[1,2-b]pyridazine (**6a**). 3-Amino-6-chloropyridazine (**3a**)[15] (13.0 g, 100 mmol) and chloroketene diethyl acetal (**4**) (15.0 g, 100 mmol) were added to 600 mL of EtOAc and heated at 75 °C for 30 min. A second equivalent of **3a** (13.0 g, 100 mmol) in 75 mL of DMF was then added in one portion to the reaction solution, and the solution was heated an additional 20 h at 75 °C. The reaction mixture was cooled in an ice bath, and the solid was collected by filtration. The solid was suspended in 100 mL of MeOH, heated to boiling and filtered hot to give 12.9 g of **5a** after drying. The filtrates were combined and evaporated to dryness. The resulting solid was washed with 50 mL of hot MeOH, from which 1.1 g of **5a** was obtained after filtration of the mixture. The filtrate was evaporated to dryness, and the residue was extracted with petroleum ether (2 x 50 mL). The combined extracts were reduced in volume to give 1.1 g of **6a**. The residue that remained from the petroleum ether extracts was suspended in H_2O, neutralized with $NaHCO_3$, heated to boiling and filtered hot. Upon cooling, 7.5 g of **3a** crystallized from the filtrate. Total yield of **5a** was 14.0 g (50%; 70% based upon unrecovered **3a**), mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 10.59 (s, 1, N-H), 8.44 (s, 1, H-3), 8.06 (d, J = 9.3 Hz, 1), 7.69 (d, J = 9.3 Hz, 1), 7.47 (d, J = 9.3 Hz, 1), 7.34 (d, J = 9.3 Hz, 1). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 284 (11), 282 (64), 280 (100, M^+), 254 (18), 252 (26), 219 (10), 217 (29). UV λ_{max} nm (ϵ x 10^3, $Lmol^{-1}$ cm^{-1}): (EtOH) 385 (br) (14.2), 260 (sh) (19.7), 255 (20.4), 220 (sh) (20.4), 215 (21.7). Calcd for $C_{10}H_6N_6Cl_2$:

C, 42.73; H, 2.15; N, 29.90. Found: C, 42.73; H, 2.38; N, 29.50.

The yield of **6a** was 1.1 g (6%), mp 113-116 °C. ^{1}H-NMR ($CDCl_3$) δ 7.62 (d, $J_{8,7}$ = 9.0 Hz, 1, H-8), 7.32 (s, 1, H-3), 6.92 (d, $J_{7,8}$ = 9.0 Hz, 1, H-7), 4.27 (q, J = 6.9 Hz, 2, CH_2), 1.39 (t, J = 6.9 Hz, 3, CH_3). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 199 (40), 198 (12), 197 (100, M^+), 171 (33), 169 (97), 134 (47), 79 (36). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1} cm^{-1}): (EtOH) 360 (7.1), 247 (6.4), 220 (12.2). Calcd for $C_8H_6ClN_3O$: C, 48.62; H, 4.08; N, 21.26. Found: C, 48.73; H, 4.06; N, 21.43.

2,9-Dichloropyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (**2a**). To a suspension of **5a** (10.0 g, 36 mmol) in 250 mL of 2,2,2-trifluoroethanol (TFE) was added dropwise a solution of iodobenzene diacetate (17.0 g, 53 mmol) in 100 mL of TFE over a period of 2 h. After an additional 30 min, the solvent was removed by rotary evaporation and the resulting residue was treated with 100 mL of hot EtOAc. The solid that resulted was collected by filtration, washed with an additional 50 mL of EtOAc, and dried to yield 5.9 g (59%) of **2a**, mp > 250 °C. Recrystallization from ethanol provided analytically pure **2a**. ^{1}H-NMR ($(CD_3)_2SO$): δ 8.47 (d, $J_{4,3}$ = $J_{7,8}$ = 9.6 Hz, 2, H-4 and 7), 7.66 (d, $J_{3,4}$ = $J_{8,7}$ = 9.6 Hz, 2, H-3 and 8). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 282 (13), 280 (64), 278 (100, M^+), 245 (16), 243 (52), 167 (16), 165 (57), 113 (27), 105 (23). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1}cm^{-1}): (EtOH) 401 (15.4), 382, (15.0), 321 (5.5), 308 (6.8), 288 (9.7), 278 (sh) (8.0), 260 (sh) (9.3), 238 (21.7), 222 (sh) (17.3). Fluorescence: λ^{em}_{max} 425.5 nm, Φ = 0.33 (absolute ethanol). Calcd for $C_{10}H_4N_6Cl_2$: C, 43.04; H, 1.44; N, 30.11. Found: C, 43.31; H, 1.58; N, 29.84.

N-(3-pyridazinyl)imidazo[1,2-b]pyridazin-2-amine (**5b**) and 2-Ethoxyimidazo[1,2-b]pyridazine (**6b**). The procedure used to obtain **5a** and **6a** was followed to afford **5b** (8%) and **6b** (14%) from **3b**.[16]

Compound **5b**: mp > 250 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 10.25 (s, 1, N-H), 8.74 (d, J = 4.2 Hz, 1), 8.53 (s, 1, H-3), 8.43 (d, J = 4.6 Hz, 1), 7.96 (d, J = 8.9 Hz, 1), 7.52 (m, 1), 7.41 (d, J = 8.9 Hz, 1), 7.20 (m, 1). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 213 (12), 212 (100, M^+), 184 (24), 183 (10), 158 (25), 157 (12). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1} cm^{-1}): (EtOH) 370 (11.7), 255 (18.5), 230 (br) (16.1), 220 (br) (15.0). Calcd for $C_{10}H_8N_6$: C, 56.60; H, 3.80; N, 39.60. Found: C, 56.34; H, 3.68; N, 39.57.

Compound **6b**: mp 52-53 °C. ^{1}H-NMR ($CDCl_3$) δ 8.22 (d, $J_{6,7}$ = 4.5 Hz, 1, H-6), 7.74 (d, $J_{8,7}$ = 8.7 Hz, 1, H-8), 7.42 (s, 1, H-3), 6.95 (dd, $J_{7,6}$ = 4.5 Hz, $J_{7,8}$ = 8.7 Hz, 1), 4.34 (q, J = 7.2 Hz, 2, CH_2), 1.47 (t, J = 7.2 Hz, 3, CH_3). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 163 (71, M^+), 135 (100), 80 (96), 79 (29), 57 (12), 53 (67), 52 (61). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1} cm^{-1}): (EtOH) 346 (7.0), 240 (9.6), 216 (17.2). Calcd for $C_8H_9N_3O$: C, 58.89; H, 5.56; N, 25.75. Found: C, 59.00; H, 5.70; N, 25.54.

Pyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]pyridazine (**2b**).

Method A. The procedure used for the synthesis of **2a** was used to obtain 65 mg of crude **2b** starting from 150 mg of **5b**. The crude material was purified using radial chromatography[18] ($CHCl_3$-MeOH, 9:1) to give 62 mg (42%) of **2b**.

Method B. Compound **2a** (1.0 g, 3.6 mmol) and 5% Pd/$CaCO_3$ (0.5 g) were suspended in 75 mL of a 2:1 solution of methyl cellosolve-DMF. The suspension was hydrogenated for 3 h at 40 psi. The resulting mixture was warmed on a steam bath and filtered hot through a pad of Celite. The filtrate was evaporated to dryness, and the residue was dissolved into 200 mL of ethanol. The volume was

reduced to 125 mL. When the concentrate was cooled, compound **2b** crystallized from solution to give, after drying, 590 mg (78%) of a pale yellow solid, mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 8.74 (dd, $J_{2,4} = J_{9,7} = 1.2$ Hz, $J_{2,3} = J_{9,8} = 4.5$ Hz, 2, H-2 and 9), 8.37 (dd, $J_{4,2} = J_{7,9} = 1.2$ Hz, $J_{4,3} = J_{7,8} = 9.4$ Hz , 2, H-4 and 7), 7.50 (dd, $J_{3,2} = J_{8,9} = 4.5$ Hz, $J_{3,4} = J_{8,7} = 9.4$ Hz, 2, H-3 and 8). FT-IR (KBr) 3020, 1625, 1605, 1570, 1495, 1485, 1470, 1320, 1255, 1235, 1165, 1130, 875, 795, 780, 730, 625 cm^{-1}. EI-Mass spectrum (70 eV) *m/z* (rel intensity): 211 (12), 210 (100, M$^+$), 117 (11). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1}cm^{-1}): (EtOH) 387 (16.7), 372 (16.7), 314 (6.4), 302 (7.3), 278 (10.0), 262 (10.3), 252 (13.0), 227 (22.2). Fluorescence: λ^{em}_{max} 420.5 nm, Φ = 0.63 (absolute ethanol). Calcd for $C_{10}H_6N_6$: C, 57.14; H, 2.88; N, 39.98. Found: C, 57.11; H, 2.91; N, 39.77.

2,9-Dimethoxypyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]pyridazine (7). Sodium (4.6 mg, 2 mmol) was dissolved in 5 mL of MeOH and compound **2a** (140 mg, 0.5 mmol) was then added. The mixture was heated at reflux for 2.5 h followed by cooling in an ice bath. The solid that separated was filtered, washed with water and methanol, and recrystallized from methanol to give 105 mg (78%) of **7**, mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 8.13 (d, $J_{4,3} = J_{7,8} = 9.9$ Hz, 2, H-4 and 7), 7.02 (d, $J_{3,4} = J_{8,7} = 9.9$ Hz, 2, H-3 and 8), 4.00 (s, 6, CH_3). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 271 (15), 270 (100, M$^+$), 255 (16). UV λ_{max} nm (ϵ x 10^3, Lmol^{-1}cm^{-1}): (EtOH) 385 (21.4), 367 (20.8), 310 (5.1), 296 (6.2), 284 (5.1), 226 (23.1), 220 (sh) (21.9). Fluorescence: λ^{em}_{max} 416.5 nm, Φ = 0.69 (absolute ethanol). Calcd for $C_{12}H_{10}N_6O_2$: C, 53.33; H, 3.73; N, 31.10. Found: C, 53.36; H, 3.69; N, 31.06.

2,9-Diazidopyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (8). Compound **2a** (1.4 g, 5 mmol) was heated with NaN_3 (0.97 g, 15 mmol) in 50 mL of DMF at 125-130 °C for 2.5 h. The solution was then cooled in an ice bath. The precipitate that resulted was collected, washed with H_2O (2 x 25 mL) and MeOH (25 mL) to give 1.1 g of **8**. H_2O (50 mL) was added to the mother liquor to give an additional 50 mg for a total yield of 1.15 g (79%) of **8** that was pure enough to be used in the synthesis of **9**, mp > 190 °C (dec). ^{1}H-NMR ($(CD_3)_2SO$) δ 8.44 (d, $J_{4,3} = J_{7,8} = 9.9$ Hz, 2, H-4 and 7), 7.27 (d, $J_{3,4} = J_{8,7} = 9.9$ Hz, 2, H-3 and 8). FT-IR (KBr) 2145, 2120, 2090. EI-Mass spectrum (70 eV) *m/z* (rel intensity): 293 (14), 292 (100, M$^+$), 270 (14), 182 (36), 128 (19), 103 (13), 102 (82), 78 (35), 51 (26).

2,9-Diaminopyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (9). Compound **8** (1.0 g, 3.4 mmol) and 5% Pd/C (0.3 g) were suspended in 100 mL of methyl cellosolve and treated with H_2 (50 psi) for 1.5 h. The mixture was filtered through Celite, and the filtrate was evaporated to dryness. The residue was suspended in 20 mL of MeOH and filtered. The resulting solid was recrystallized from DMF-MeOH and dried to give 0.86 g (98%) of **9**, mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 7.88 (d, $J_{4,3} = J_{7,8} = 9.9$ Hz, 2, H-4 and 7), 683 (d, $J_{3,4} = J_{8,7} = 9.9$ Hz, 2, H-3 and 8), 6.52 (s, 4, NH_2). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 241 (14), 242 (100, M$^+$). High resolution EI-Mass spectrum: *m/z* found 240.0880 ($C_{10}H_8N_8$) requires 240.0872. UV λ_{max} nm (ϵ x 10^3, Lmol^{-1}cm^{-1}): (EtOH) 394 (sh) (18.4), 380 (22.6), 318 (6.4), 304 (6.4), 276 (5.6), 242 (28.2), 230 (sh) (26.0). Fluorescence: λ^{em}_{max} 449.5 nm, 470.5 nm Φ = 0.19 (absolute ethanol). Calcd for $C_{10}H_8N_8 \cdot 1.0\ H_2O$: C, 46.51; H, 3.90; N, 43.39. Found: C, 47.25; H, 3.39; N, 43.28.

2,9-Dihydrazinopyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (10). Compound **2a** (0.2 g, 0.7 mmol) was treated with anhydrous hydrazine (2 mL) for 80 h at room temperature. The precipitate was collected, washed with water and methanol, recrystallized from DMSO-H_2O, and dried to give 0.18 g (92%) of **10**, mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$) δ 8.02 (s, 2, NH), 7.82 (d, $J_{4,3} = J_{7,8} = 9.9$ Hz, 2, H-4 and 7), 6.40 (d, $J_{3,4} = J_{8,7} = 9.9$ Hz, 2, H-3 and 8), 4.29 (s, 4, NH_2). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 271 (14), 270 (100, M^+), 255 (29), 240 (39), 225 (15), 120 (13), 79 (11). High resolution EI-Mass spectrum: *m/z* found 270.1089 ($C_{10}H_{10}N_{10}$) requires 270.1090. UV λ_{max} nm ($\epsilon \times 10^3$, $Lmol^{-1}cm^{-1}$): (EtOH) 394 (sh) (16.9), 382 (18.0), 318 (6.1), 306 (6.1), 280 (6.8), 236 (22.7). Fluorescence: λ^{em}_{max} 428.0 nm, 463.0 nm Φ = 0.06 (absolute ethanol). Calcd for $C_{10}H_{10}N_{10}\cdot 1.0\ H_2O$: C, 41.67; H, 3.80; N, 48.59. Found: C, 41.91; H, 3.80; N, 48.94.

2,9-Dibenzyloxypyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (11). Sodium (0.7 g, 30 mmol) was dissolved in 25 mL of benzyl alcohol. The solution was then heated to 80 °C and compound **2a** (2.0 g, 7.2 mmol) was added. The mixture was heated at 80 °C for an additional 3 h and then cooled in an ice bath. The solid that separated was filtered and washed with 10 mL of 50% aqueous EtOH followed by 10 mL of H_2O. The dried compound was recrystallized from $CHCl_3$-hexane to yield 2.4 g (79%) of **11**, mp > 260 °C. ^{1}H-NMR ($CDCl_3$) δ 8.03 (d, $J_{4,3} = J_{7,8} = 9.8$ Hz, 2, H-4 and 7), 7.64 and 7.41 (m, 10, phenyl), 6.95 (d, $J_{3,4} = J_{8,7} = 9.8$ Hz, 2, H-3 and 8), 5.56 (s, 4, CH_2). EI-Mass spectrum (70 eV) *m/z* (rel intensity): 423 (19), 422 (71, M^+), 91 (100). UV λ_{max} nm ($\epsilon \times 10^3$, $Lmol^{-1}\ cm^{-1}$): (EtOH) 389 (23.9), 371 (23.7), 312 (7.0), 298 (7.5), 270 (6.9), 238 (33.3), 206 (42.7). Calcd for $C_{24}H_{18}N_6O_2$: C, 68.24; H, 4.29; N, 19.89. Found: C, 68.30; H, 4.33; N, 20.06.

2,9-Dihydroxypyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]-pyridazine (12). Compound **11** (0.5 g, 1.2 mmol) was added to 10 mL of 48% HBr and the mixture was heated at reflux for 40 min. The resulting solution was cooled in an ice bath. The white solid that precipitated was collected by filtration and washed with 10 mL of ether. The solid was stirred with 10 mL of a saturated aqueous $NaHCO_3$ solution for 15 min. The pale green solid that separated was collected by filtration, washed with water, and suspended in hot ethanol. The insoluble material was collected by filtration and dried to afford 185 mg (64%) of **12**, mp > 260 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 7.61 (d, J = 9.9 Hz, 2), 6.53 (d, J = 9.9 Hz, 2). FT-IR (KBr) 3420, 1610, 1590, 1550, 1435, 1265, 820 cm^{-1}. EI-Mass spectrum (70 eV) *m/z* (rel intensity): 244 (17), 243 (13), 242 (100, M^+). High resolution EI-Mass spectrum: *m/z* found 242.0554 ($C_{10}H_6N_6O_2$) requires 242.0552. UV λ_{max} nm: (EtOH) 400 (sh), 378, 320, 275, 234. Fluorescence: λ^{em}_{max} 439.0 nm, 465.0 nm Φ = 0.06 (absolute ethanol). Calcd for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50. Found: C, 49.79; H, 2.55.

Preparation of Cobalt(II) Complexes. General Procedure. A solution of cobalt(II) chloride hexahydrate (0.12 mmol in 4 mL of EtOH) was added to a hot solution of the heterocycle (0.24 mmol in 50 mL of EtOH). The resulting mixture was heated at reflux for an additional 5 min and allowed to stand overnight. The blue precipitate was collected by filtration and dried under vacuum at 110 °C for 72 h.

Bis(pyridazo[2",3":1',2']imidazo[4',5':4,5]imidazo[1,2-b]pyridazine) cobalt(II) Chloride. 44% yield, mp > 260 °C. Calcd for $C_{20}H_{12}N_{12}Cl_2Co$: C, 43.66; H, 2.20; N, 30.55; Cl, 12.89; Co, 10.71. Found: C, 43.61; H, 2.22;

N, 30.54; Cl, 13.12; Co, 10.50.

Bis(pyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine)cobalt(II) Chloride. 48% yield, mp > 260 °C. Calcd for $C_{34}H_{18}N_8Cl_2Co \cdot 0.5\ H_2O$: C, 51.91; H, 3.09; N, 20.18; Cl, 12.77; Co, 10.61. Found: C, 52.17; H, 2.99; N, 20.05; Cl, 12.64; Co, 10.64.

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