**Methylation of 12d and 13d.** A solution of **12d** (1.59 g, 10 mmol) in 20 mL of dry acetonitrile was added to trimethyloxonium fluoroborate (1.50 g) in 30 mL of dichloromethane and 10 mL of acetonitrile at −20 °C. After the mixture was stirred for 1 h, the solvent was evaporated, and the residue was washed with anhydrous ether. Hydrolysis to acetaldehyde was noted, and the product failed to crystallize. No simple proton or carbon NMR spectrum was obtained. A comparable procedure with **13d** (0.68 g, 5 mmol) gave crystalline material (1.14 g, 96%), assigned as **13g**, mp 87–97 °C. $^1$H NMR ($CD_3NO_2$): δ (ppm) 2.1–2.4 (m, $CH_2$), 2.36 (s, $CH_3CO$), 2.90 and 2.97 (s, $S^+CH_3$), 3.5 and 3.8 (m, $CH_2S$), 3.85 and 4.12 (m, $CH_2N$), 5.17–5.71 (m, $SCH_2N$). For $^{13}$C NMR data, see supplementary material.

The salt mixture obtained from the methylation of **12d** was treated with 50 mL of methanol containing 1% w/v of potassium *tert*-butoxide. After 1 h of stirring the solvent was evaporated, and the neutral products were extracted with ether (20 mL), dried, and evaporated to give a straw-colored liquid. GPLC analysis gave three peaks. Separation and analysis by NMR identified the major product as *N*-[3-(methylthio)propyl]acetamide **16a**, some starting material **12d**, and a new compound, which, by NMR and MS analysis, is assigned the structure *N*-[3-(methylthio)-propyl]-*N*-(1-methoxyethyl)acetamide (**12h**). Via the same procedure, salt **13g** (1.0 g) gave with methanol and 1% KOBu$^t$ neutral products, one component of which is assigned the structure *N*-[3-(methylthio)propyl]-*N*-(methoxymethyl)acetamide (**13h**) (see supplementary material).

**Methylthiolation of Tetrahydro-1,3-thiazines 12d, 13d, 14a, and 15a.** To **12d** (0.386 g, 2.42 mmol) in dry nitromethane (5 mL) was added dimethyl(methylthio)sulfonium fluoroborate (**5**)[10] (0.477 g, 2.43 mmol) all at once. After the mixture was stirred for 3 h at room temperature, the volatile products ($Me_2S$ and MeSSMe) and solvent were removed by evaporation at reduced pressure. Part of the residue was redissolved ($CD_3NO_2$) and analyzed by $^1$H and $^{13}$C NMR spectroscopy. Another part of the residue was dissolved in dilute potassium carbonate and extracted with chloroform, and the extract was examined by NMR. The same procedure was applied to **13d**. The results of the analysis are described in the Results and Discussion. In the case of **15a** and **14a**, 50 mmol of the thiazine derivative in 20 mL of dichloromethane was treated with 50 mmol of **5** (which is very slightly soluble in dichloromethane) at room temperature. After 3 h of stirring, the solvent and methyl sulfide were removed at reduced pressure, and the viscous residue was analyzed by NMR spectroscopy. The results are described in the Results and Discussion.

**Registry No.** **1**, 33696-21-8; **2**, 20280-45-9; **3**, 35332-10-6; **6a**, 118515-34-7; **6b**, 74500-21-3; **7**, 87094-61-9; **8**, 74484-54-1; **9**, 74484-26-7; **10**, 87094-23-3; **11**, 109857-46-7; **12a**, 73317-67-6; **12a**·HCl, 79128-35-1; **12b**, 15047-09-3; **12d**, 118515-27-8; **12e**, 118515-25-6; **12g**, 118515-33-6; **12h**, 118515-30-3; **13a**, 543-21-5; **13a**·HCl, 79128-34-0; **13d**, 118515-26-7; **13g**, 118515-29-0; **13h**, 118515-31-4; **14a**, 76888-71-6; **14j**, 118537-30-7; **15a**, 60035-84-9; **15a**·HCl, 118515-24-5; **15j**, 118515-35-8; **16a**, 54824-91-8; **16b**, 81645-14-9; **17**, 118515-36-9; $HO(CH_2)_3NHAc$, 10601-73-7; $HO(CH_2)_3NH_2$, 156-87-6; $C_6H_5CH_2SH$, 100-53-8; $C_6H_5CH_2S(CH_2)_2CO_2CH_3$, 5331-36-2; $CH_3NH_2$, 74-89-5; $C_6H_5CH_2S(CH_2)_2CONHCH_3$, 56788-03-5; $C_6H_5CH_2S(CH_2)_3NHCH_3$, 118515-22-3; $HS(CH_2)_3NHCH_3$·HCl, 118515-23-4; $H_2C{=}CHCO_2CH_3$, 96-33-3; $Me_4N^+I^-$, 75-58-1; $Me_2N^+Et_2I^-$, 4325-24-0; methanesulfenyl chloride, 5813-48-9; dimethylamine, 124-40-3; methyl disulfide, 624-92-0; ethyl iodide, 75-03-6; 1-(*N*,*N*-dimethylamino)-2-chloroethane, 107-99-3; sodium methanethiolate, 5188-07-8; chloromethyl methyl sulfide, 2373-51-5; 3-mercapto-1-propylamine hydrochloride, 7211-54-3; acetaldehyde, 75-07-0.

**Supplementary Material Available:** $^{13}$C NMR chemical shifts for **12d**, **12g**, **12h**, **13d**, **13g**, **13h**, **14j**, **15j**, **16b**, and **17** (3 pages). Ordering information is given on any current masthead page.

# Polyaza-Cavity Shaped Molecules. 14. Annelated 2-(2′-Pyridyl)indoles, 2,2′-Biindoles, and Related Systems

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*Received July 15, 1988*

The Fisher indole synthesis has been employed with a series of α-keto-2,3-cycloalkenopyridines to provide 3,3′-polymethylene bridged derivatives of 2-(2′-pyridyl)indole. The same reaction with α,α′-diketo[2,3:5,6]dicycloalkenopyridines provides bis-annelated derivatives of 2,6-di(2′-indolyl)pyridine. With 1,2-cycloalkanediones one obtains a mixture of two products resulting from one or two successful Fisher cyclizations. The cage diketone, tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione, affords a molecule with two indole rings arranged as a *syn*-orthocyclophane. UV absorption and hydrogen bonding are found to vary as a function of the planarity of the molecule while cyclopalladation occurs readily regardless of conformation.

## Introduction

Over the past several years we have been interested in the study of bridged azabiaryl systems in which a polymethylene bridge may be used to control the conformation of the interior cavity of the molecule. The resulting 2,2′-bipyridines,[1] 2,2′;6′,2″-terpyridines,[2] and their related dibenzo- and dipyrido-fused analogues[3] have been investigated as ligands in forming complexes with a variety of transition metals.[4]

Our strategy in the synthesis of these materials has centered around the selection of appropriately oriented ketones or diketones. These compounds were then allowed to react with an *o*-amino aldehyde via the Friedländer condensation[5] to provide the corresponding pyridine, quinoline, or 1,8-naphthyridine system. In this work we will expand this approach, using the same carbonyl compounds to provide derivatives of 2-(2′-pyridyl)indole, 2,2′-biindole, and other related compounds.

From a conceptual point of view, 2-(2′-pyridyl)indole (1) may be considered a lower homologue of 2-(2′-pyridyl)-

(1) Thummel, R. P.; Lefoulon, F.; Mahadevan, R. *J. Org. Chem.* **1985**, *50*, 3824.
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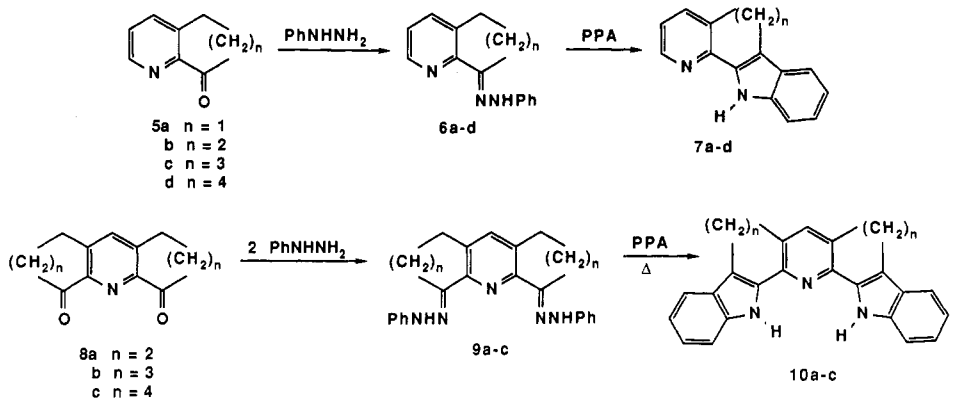
**Scheme I**



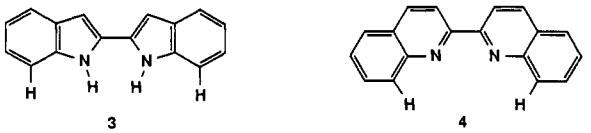

quinoline (**2**). As a potential ligand the binding properties of **1** will be affected in three ways. One can approximate the bite angle ($\alpha$) of a bidentate ligand by considering the

**1** **2**

intersection of the linear axes of the orbitals containing the donor electrons. As this angle becomes larger, the intersection moves closer to the ligand, better approximating the orthogonal orientation preferred for octahedral complexation. For **1** the five-membered pyrrole ring leads to a smaller, less favorable angle $\alpha$, and the apex of the two coordination axes is displaced toward the indole ring.

For 2-(2′-pyridyl)quinoline and, more importantly, 2,2′-biquinoline (**4**), we have discovered that the C-8 hydrogen points toward the chelating site and can impede coordination. Thus octahedral complexes of the type $M(4)_3$ are sometimes difficult to prepare. This steric problem is partially alleviated in **1** and **3** where $H_7$ is directed more away from the coordination site.

Lastly, azabiaryls such as bipyridine and biquinoline are neutral ligands that do not influence the overall charge of a metal complex. For **1** to form a chelate ring, it must first deprotonate, giving the ligand a negative charge and thus lowering the overall charge of the resulting complex.



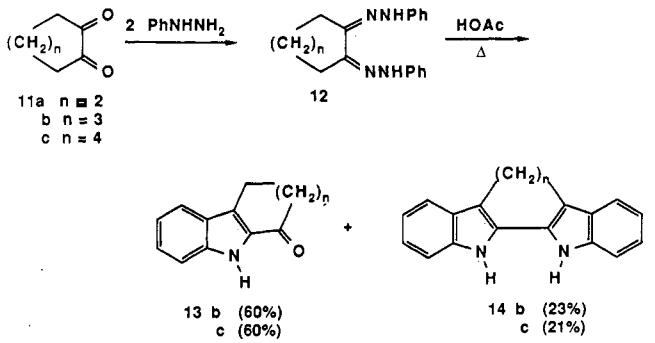
**3** **4**

The synthesis of the parent system, **1**, by the Fisher reaction of the phenylhydrazone of 2-acetylpyridine was reported by Caixach and co-workers.[6] The IR and UV properties of the molecule have also been presented.[7] The 2,2′-biindole system (**3**) has been studied somewhat more extensively. The parent system or substituted derivatives have been prepared either by electrophilic substitution with indolin-2-one,[8] reductive dimerization of a 3,3′-bridged biindole,[9] Ullmann coupling of 2-haloindoles,[10] or a double Fisher reaction on the bis(hydrazone) of a 1,2-diketone.[11] The latter reaction proceeds in a stepwise or concerted fashion, depending on the choice of reaction conditions. The steric and electronic considerations discussed for **1** would be even more apparent when comparing **3** with 2,2′-biquinoline (**4**).

## Synthesis

The indole derivatives described in this work were all prepared by a straightforward application of the Fisher indole synthesis[12] (see Scheme I). Phenylhydrazones and bis(phenylhydrazones) were synthesized in good yields from the corresponding ketones and diketones by reaction with phenylhydrazine. These materials were then treated with polyphosphoric acid at 100 °C or refluxing acetic acid to provide the indole derivatives. Characterization of these materials by $^1H$ NMR was readily accomplished due to the existence of discrete spin systems involving the benzo, pyridyl, and polymethylene bridge protons.[13]

The hydrazone precursors to **7** and **10** may be considered as activated in the sense that they are conjugated to a pyridine ring. Unactivated systems do not undergo the Fisher reaction as readily as activated ones. When the bis(hydrazones) derived from diketones **11b** and **11c** are treated with PPA they give none of the expected bis(indoles). As has been shown previously for 1,2-cyclohexanedione (**11a**), the employment of milder conditions, such as refluxing acetic acid, leads to the isolation of ketoindole **13** as a major product accompanied by some of the desired bis(indole) **14**.[11a] The ketones **13** would be useful substrates for Friedländer condensations with *o*-amino aldehydes that could provide bridged derivatives of indole-substituted quinolines or 1,8-naphthyridines.




Another type of diketone that is a good starting point for the preparation of oriented azabiaryl systems is tet-

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(9) Bergman, J.; Pelcman, B. *Tetrahedron Lett.* **1987**, *28*, 4441.
(10) Bergman, J.; Eklund, N. *Tetrahedron* **1980**, *36*, 1439.
(11) (a) Moldenhauer, W.; Simon, H. *Chem. Ber.* **1969**, *102*, 1198. (b) Mann, F. G.; Willcox, T. J. *J. Chem. Soc.* **1958**, 1525.
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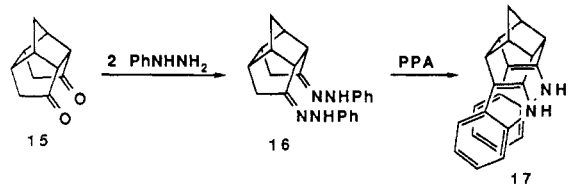
(13) Ezell, E. L.; Thummel, R. P.; Martin, G. E. *J. Heterocycl. Chem.* **1984**, *21*, 817.

Table I. N-H Chemical Shifts[a] and Ultraviolet Absorption Data[b] for 2-(2′-Pyridyl)indoles

| compd | δ(N-H) | $\lambda_{max}$ (ε) |
|---|---|---|
| 1 | 11.91 | 246 (6750) 325 (18000) |
| 7a | 10.48 | 247 (6600) 334 (20300) |
| 7b | 11.91 | 248 (8450) 342 (18700) |
| 7c | 10.02 | 247 (7200) 332 (15200) |
| 7d | 9.32 | 249 (8000) 317 (12300) |
| 18 | 7.74 | |

[a] Recorded at 300 MHz for approximately 1% solutions in $CDCl_3$ with chemical shifts in ppm downfield from $Me_4Si$. [b] Wavelength in nm for $1.79 \times 10^{-4}$ M solutions in 95% EtOH.

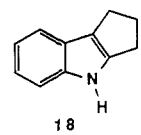
racyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione (**15**). The bis(hydrazone) **16** forms readily in 94% yield and treatment with PPA converts it into the *syn*-orthocyclophane system **17** in 68% yield. Elemental analysis indicates the presence of one molecule of $NH_3$ bound to **17**.




15 16 17

## Properties

Pyridylindoles **7** are capable of exhibiting intramolecular H-bonding between the indole N–H and the pyridine lone pair electrons. The degree of H-bonding should vary as a function of the length of the polymethylene bridge and can be evaluated by consideration of the N–H chemical shift. Table I lists these resonances for the series of 2-(2′-pyridyl)indoles as well as 2,3-trimethyleneindole (**18**),




18

which is included as an example of an indole that cannot H-bond intramolecularly. Increased H-bonding, as indicated by a downfield shift of the N–H resonance, is clearly greatest for compounds **1** and **7b**. As the bridge is increased to three and four carbons, the N–H signal moves upfield so that **7d** shows the least H-bonding. It is interesting to note that although the estimated distance between the indole proton and the pyridine nitrogen in **7a** and **7d** is quite similar, H-bonding appears to be more important for the monomethylene bridged system. For **7a** the bridging N–H bond lies in the plane of the pyridine ring, demonstrating that orientation as well as proximity of the H-bonding lone pair electrons is important for effective participation.

In earlier papers we have examined the effect of 3,3′-bridging on the conformations of 2-(2′-pyridyl)quinoline (**2**)[3c] and 2,2′-biquinoline (**4**).[3b] In both cases we observed that the systems with two and three carbon bridges are conformationally mobile. Rotation about the 2,2′ bond is accompanied by conformational inversion of the polymethylene bridge such that the geminal methylene protons are equivalent at room temperature on the NMR time scale. Under similar conditions, systems with a tetramethylene bridge are conformationally rigid and show nonequivalence of these geminal methylene protons.

The situation is somewhat different for the indole derivatives **7** and **14**. All three bridged derivatives **7b,c,d** now appear conformationally mobile by NMR. Whereas the 3,3′-tetramethylene derivative of **2** shows eight different proton resonances in the region of 1.5–3.0 ppm, **7d** shows two two-proton benzylic signals at 2.82 and 3.0 ppm and a broad four-proton peak at 1.77 ppm. Two factors help to account for this increased flexibility. The 3,3′-distance in **1** is slightly more than that in **2**, so that less twisting is needed to accommodate a four-carbon bridge. Furthermore, H-bonding in **7d** effectively creates a one-atom bridge between the two nitrogens, which helps to flatten the molecule and decrease the rotational barrier.

For the tetramethylene-bridged 2,2′-biindole **14c**, the 3,3′ distance is even greater but the H-bonding interaction is absent. In fact, one might expect a small amount of NH–NH repulsion. The NMR spectrum of **14c** shows two broad signals at 1.92 and 3.02 ppm for the benzylic and nonbenzylic methylene protons. When the sample is cooled to −65° C, we see broadening of these signals but they do not separate into the expected nonequivalent geminal methylene resonances characteristic of conformational rigidity. We estimate the inversion barrier to be less than 11 kcal/mol.

The layered bis(indole) **17** shows spectroscopic properties that are analogous to those of the corresponding bis(quinoline) derivative reported earlier.[14] The aromatic proton resonances in **17** are shielded by about 0.5–0.8 ppm as compared to those of 2,3-trimethyleneindole (**18**). These shifts are about twice what is observed for the bis(quinoline) derivative and probably reflect a somewhat lesser interplanar distance between the benzo rings of **17**. The UV absorption maximum for **17** occurs at 285 nm (ε 6650), which is 5 nm greater than that observed for **18**. Again this effect is somewhat greater than that in the quinoline analogue.

The ultraviolet absorption spectra of **7a–d** were measured in 95% EtOH and the two long wavelength absorption bands are included in Table I. In considering these bands, two trends become obvious. Along the series **7b,c,d**, the absorption maximum shifts from 342 to 317 nm while the intensity of the peak decreases. Both trends are consistent with an increase in the dihedral angle between the two aromatic rings, which causes a diminished resonance delocalization in the system. Considering the absorption maximum of 325 nm for the unbridged system **1**, we can estimate its conformation to be intermediate between that of **7c** and **7d**. The monomethylene-bridged system shows a higher energy absorption than we might predict. Due to the strain embodied in the five-membered ring of **7a**, the π-character of the 2,2′ bond is probably diminished, leading to less delocalization for this species.

## Cyclometalation

In accord with our original premise for this study, it became of interest to determine the utility of 2-(2′-pyridyl)indoles as potential ligands. In an earlier study we had investigated the cyclopalladation of polymethylene-bridged derivatives of 2-phenylpyridine.[15] This reaction occurs smoothly and proceeds by a mechanism that is presumed to involve initial coordination of the pyridyl nitrogen with the palladium species followed by electrophilic attack and deprotonation at the ortho position of the phenyl ring.[16] We reasoned that the indole rings of **1** and **7** should be quite susceptible to electrophilic attack and thus these systems might undergo cyclometalation. Treatment of palladium 2,4-pentanedionate with 1 equiv of **7a–d** provided **19a–d**, which were identified

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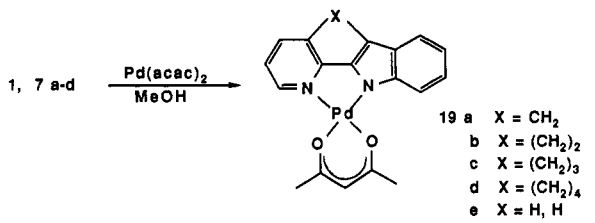
(16) (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

by $^1H$ NMR and elemental analysis. It is interesting to note that cyclopalladation is not retarded by noncoplanarity of the pyridine and indole rings in **7**. In fact, the best yield (97%) is obtained for the least planar substrate, **7d**, while the most planar system (**7a**) proceeds in only 32% yield. A similar observation was made for the previously examined bridged derivatives of 2-phenylpyridine.[15] In that series, 4-azafluorene would not cyclopalladate at all.




Normally indole prefers electrophilic substitution at the 3-position while the 1-position is clearly less reactive.[17] Systems **7a–d** leave no choice as to the site of attack by palladium but the unbridged analogue **1** could possibly cyclopalladate at the 3-position. The reaction proceeded smoothly in 86% yield to provide a product in which the N–H resonance was again absent, implying the formation of **19e**. This assignment was reinforced by the observation of a singlet at 6.92 ppm for $H_3$, which appears at 7.00 in the free ligand. Furthermore, no imine absorption appeared in the IR spectrum of **19e**. The series **10a–c** should provide interesting substrates for cyclopalladation and these are currently under investigation.

In a preliminary study, we treated **7b** with *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O, where bpy = 2,2′-bipyridine, followed by ammonium hexafluorophosphate. A complex was obtained in 36% yield, which $^1H$ NMR and FAB mass spectral analysis indicated to be Ru(bpy)$_2$(**7b**)[PF$_6$]. Unlike most Ru(bpy)$_2$L$^{+2}$ complexes, this species is monovalent and is expected to manifest some interesting properties.[4c] Its chemistry will be presented in future work.

## Experimental Section

Nuclear magnetic resonance spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for $^1H$ and 75 MHz for $^{13}C$, and chemical shifts are reported in parts per million downfield from $Me_4Si$. Infrared spectra were obtained on a Perkin-Elmer 1330 spectrometer. Ultraviolet spectra were obtained on a Perkin-Elmer 330 spectrophotometer. FAB mass spectra (*m*-nitrobenzyl alcohol matrix) and high resolution mass spectra were obtained on a VG 70-SEQ mass spectrometer. All solvents were freshly distilled reagent grade and all melting points are uncorrected. A literature procedure was used to prepare 2,3-trimethyleneindole (**18**).[18] Elemental analyses were performed by Canadian Microanalytical Service, Ltd., New Westminster, B.C.[19]

**General Procedure for Phenylhydrazone Preparation.** The ketone or diketone was combined with 1 or 2 equiv of freshly distilled phenylhydrazine in a small volume of absolute ethanol (ca. 10 mL) and heated on a steam bath for 30 min. After cooling the red solution to room temperature, the resulting yellow crystals were collected by suction filtration, washed with cold ethanol (5–10 mL), and dried under vacuum.

**Phenylhydrazone of 2-Acetylpyridine.** The reaction of 5.0 g (.04 mol) of 2-acetylpyridine with 4.47 g (.04 mol) of phenylhydrazine provided 8.5 g (96%) of 2-acetylpyridine phenylhydrazone, mp 152–154 °C (lit.[20] mp 149–154 °C): $^1H$ NMR ($CDCl_3$) $\delta$ 8.53 (d, $H_6$, $J$ = 4.4 Hz), 8.17 (d, $H_3$, $J$ = 8.1 Hz), 7.64 (t, $H_4$, $J$ = 7.5 Hz), 7.55 (bs, NH), 7.3 (m, 2 H, ArH), 7.17 (m, 3 H, $H_5$ + ArH), 6.89 (t, *p*-ArH), 2.36 (s, $CH_3$); IR (KBr) 3180, 1540, 1450, 1410, 1280, 1130, 1060, 780 cm$^{-1}$.

**Phenylhydrazone of 6,7-Dihydro-5*H*-1-pyrindin-7-one (6a).** The reaction of 0.31 g (2.1 mmol) of 6,7-dihydro-5*H*-1-pyrindin-7-one[3a] (**5a**) with 0.23 g (2.1 mmol) of phenylhydrazine provided 0.45 g (91%) of **6a**, mp 218–221 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 8.56 (d, $H_2$, $J$ = 4.5 Hz), 7.58 (d, $H_4$, $J$ = 7.5 Hz), 7.33 (bs, NH), 7.24 (d, ArH, 4 H, $J$ = 4 Hz), 7.12 (dd, $H_3$, $J$ = 4.5, 7.0 Hz), 6.87 (m, *p*-ArH), 3.11 (t, 2 H), 2.82 (m, 2 H); IR (KBr) 3280, 1600, 1570, 1450, 1430, 1240, 1150, 810, 770, 710 cm$^{-1}$.

**Phenylhydrazone of 5,6,7,8-Tetrahydro-8-quinolone (6b).** The reaction of 1.0 g (6.2 mmol) of 5,6,7,8-tetrahydro-8-quinolone[3a] (**5b**) with 0.67 g (6.2 mmol) of phenylhydrazine provided 1.5 g (97%) of **6b**, mp 184–185 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 8.57 (d, $H_2$, $J$ = 4.3 Hz), 7.75 (bs, NH), 7.42 (d, $H_4$, $J$ = 7.4 Hz), 7.24 (d, ArH, 4 H, $J$ = 3.9 Hz), 7.10 (dd, $H_3$, $J$ = 4.5, 7.5 Hz), 6.87 (m, *p*-ArH), 2.75 (t, 2 H, $J$ = 5.9 Hz), 2.69 (t, 2 H, $J$ = 6.5 Hz), 1.96 (quintet, 2 H); IR (KBr) 3210, 1600, 1570, 1550, 1500, 1450, 1430, 1250, 1150, 750 cm$^{-1}$.

**Phenylhydrazone of Cyclohepta[*b*]pyridin-9-one (6c).** The reaction of 0.75 g (4.33 mmol) of cyclohepta[*b*]pyridin-9-one[3a] (**5c**) with 0.47 g (4.33 mmol) of phenylhydrazine provided 1.04 g (91%) of **6c**, mp 211–213 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 8.59 (d, $H_2$, $J$ = 4.3 Hz), 7.56 (bs, NH), 7.43 (d, $H_4$, $J$ = 7.4 Hz), 7.22 (m, 5 H, $H_3$ and ArH), 6.90 (t, *p*-ArH, $J$ = 6.9 Hz), 2.76 (t, 2 H, $J$ = 6.4 Hz), 2.61 (m, 2 H), 1.85 (m, 2 H), 1.76 (m, 2 H); IR (KBr) 3200, 1590, 1560, 1480, 1420, 1240, 1130, 1070, 1050, 1030, 800, 750, 680 cm$^{-1}$.

**Phenylhydrazone of Cycloocta[*b*]pyridin-10-one (6d).** The reaction of 0.62 g (3.3 mmol) of cycloocta[*b*]pyridin-10-one[1] (**5d**) with 0.36 g (3.3 mmol) of phenylhydrazine provided a thick yellow oil, which was recrystallized from diethyl ether to afford 0.82 g (90%) of **6d**, mp 124–127 °C. The $^1H$ NMR spectrum showed **6d** to be a 1:1 mixture of syn and anti hydrazones, which were characterized as a mixture: $^1H$ NMR ($CDCl_3$) $\delta$ 8.60 (d, $H_2$, $J$ = 4.3 Hz), 8.51 (d, $H_2$, $J$ = 4.3 Hz), 7.63 (bs, NH), 7.60 (d, $H_4$, $J$ = 8.2 Hz), 7.52 (d, $H_4$, $J$ = 7.5 Hz), 7.2 (m, 4 H, ArH), 6.96 (d, 1 H, $J$ = 7.9 Hz), 6.80 (m, 1 H), 2.7 (m), 1.65 (m); IR (KBr) 2900, 2830, 1582, 1485, 1424, 1240, 1115, 790, 735, 680 cm$^{-1}$.

**Bis(phenylhydrazone) of 2,6-Diacetylpyridine.** The reaction of 1.0 g (6.1 mmol) of 2,6-diacetylpyridine and 1.32 g (12.2 mmol) of phenylhydrazine provided 1.95 g (94%) of the bis(hydrazone), mp 208–211 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 8.07 (d, $H_{3,5}$, $J$ = 8.1 Hz), 7.66 (t, $H_4$, $J$ = 7.2 Hz), 7.52 (bs, NH), 7.33–7.20 (m, 4 H, ArH), 6.90 (t, *p*-ArH, $J$ = 7.2 Hz), 2.44 (s, 6 H, $CH_3$), 1.60 (bs, NH); IR (KBr) 3350, 1560, 1500, 1440, 1250, 1160, 750 cm$^{-1}$.

**Bis(phenylhydrazone) of 1,8-Dioxo-1,2,3,4,5,6,7,8-octahydroacridine (9a).** The reaction of 0.50 g (2.3 mmol) of 1,8-dioxo-1,2,3,4,5,6,7,8-octahydroacridine[2] (**8a**) and 0.50 g (4.6 mmol) of phenylhydrazine provided 0.52 g (60%) of the bis(hydrazone) **9a**, mp 175–176 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 10.03 (s, NH), 7.64 (s, $H_4$), 7.4–6.7 (overlapping m, 10 ArH), 2.78 (2 overlapping m, 8 H) 2.15 (bs, NH), 2.0 (m, 4 H); IR (KBr) 3350, 2960, 1610, 1570, 1510, 1250, 1160, 1110, 1080, 760, 700 cm$^{-1}$.

**Bis(phenylhydrazone) of α,α′-Dioxo-2,3:5,6-bis(pentamethylene)pyridine (9b).** The reaction of 0.10 g (0.41 mmol) of α,α′-dioxo-2,3:5,6-bis(pentamethylene)pyridine[2] (**8b**) with 0.09 g (0.82 mmol) of phenylhydrazine provided 0.11 g (64%) of the bis(hydrazone) **9b**, mp 225–228 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 12.68 (bs, NH), 7.59 (s, $H_4$), 7.4–6.7 (overlapping m, 10 ArH), 2.9–2.6 (m, 8 H), 2.0–1.5 (m and bs, 8 H + NH); IR (KBr) 3200, 3090, 2980, 1610, 1500, 760, 700 cm$^{-1}$.

**Bis(phenylhydrazone) of α,α′-Dioxo-2,3:5,6-bis(hexamethylene)pyridine (9c).** The reaction of 0.148 g (0.54 mmol) of α,α′-dioxo-2,3:5,6-bis(hexamethylene)pyridine[2] (**8c**) with 0.122 g (1.13 mmol) of phenylhydrazine provided 0.180 g (74%) of the bis(hydrazone) **9c**, mp 146–148 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 7.44 (bs, NH), 7.35 (s, $H_4$), 7.28–7.06 (overlapping m, 8 ArH), 6.82 (t, 2 ArH, $J$ = 7.2 Hz), 2.79–2.69 (m, 8 H), 1.74–1.60 (m, 8 H + NH); IR (KBr) 2940, 1605, 1415, 1260, 760 cm$^{-1}$.

**1,2-Cycloheptanedione Bis(phenylhydrazone) (12b).** The reaction of 0.80 g (6.3 mmol) of 1,2-cycloheptanedione[21] with 1.36

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(18) Perkin, W. H.; Plant, S. G. P. *J. Chem. Soc.* **1923**, 3242.
(19) Elemental analysis were obtained for cyclopalladated derivatives, which recrystallized more readily.
(20) Sugasawa, S.; Terashima, M.; Kanaoka, Y. *Chem. Pharm. Bull.* **1956**, *4*, 16.

g (12.6 mmol) of phenylhydrazine provided a crude product that was recrystallized from ethanol to provide 1.76 g (92%) of **12b**, mp 130–134 °C; $^1$H NMR ($CDCl_3$) $\delta$ 12.59 (bs, NH), 7.48 (bs, NH), 7.33 (t, 2 H, $J$ = 7.6 Hz), 7.25 (t, 2 H, $J$ = 7.6 Hz), 7.15 (d, 2 H, $J$ = 7.8 Hz), 7.05 (d, 2 H, $J$ = 7.9 Hz), 6.94 (t, 1 H, $J$ = 7.2 Hz), 6.83 (t, 1 H, $J$ = 7.1 Hz), 2.68 (bs, 2 H), 2.52 (bs, 2 H), 1.70 (bs, 6 H); IR (KBr) 3340, 3140, 2920, 1570, 1490, 1245, 1155, 1050 cm$^{-1}$.

**1,2-Cyclooctanedione Bis(phenylhydrazone) (12c).** The reaction of 0.52 g (3.7 mmol) of 1,2-cyclooctanedione[22] and 0.80 g (7.4 mmol) of phenylhydrazine provided a crude product that was recrystallized from ethanol to provide 0.89 g (76%) of **12c**, mp 111–114 °C: $^1$H NMR ($CDCl_3$) $\delta$ 12.93 (bs, NH), 7.55 (bs, NH), 7.35 (t, 2 H, $J$ = 7.5 Hz), 7.26 (t, 2 H, $J$ = 7.5 Hz), 7.17 (d, 2 H, $J$ = 7.7 Hz), 7.07 (d, 2 H, $J$ = 7.9 Hz), 6.95 (t, 1 H, $J$ = 7.2 Hz), 6.83 (t, 1 H, $J$ = 6.8 Hz), 2.68 (m, 4 H), 1.72 (bs, 4 H), 1.54 (bs, 4 H); IR (KBr) 3420, 2920, 1580, 1500, 1245, 1100, 900, 750 cm$^{-1}$.

**2,7-Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecanedione Bis(phenylhydrazone) (16).** The reaction of 0.42 g (2.25 mmol) of tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione[23] (**15**) with 0.487 g (4.51 mmol) of phenylhydrazine provided 0.750 g (94%) of the bis(hydrazone) **16** as pale yellow crystals, mp 159–162 °C: $^1$H NMR ($CDCl_3$) $\delta$ 7.15–6.69 (overlapping m, 10 ArH), 3.11–3.05 (m, $H_{2,8}$), 2.57–2.23 (m, 8 H + NH), 1.80 (s, NH), 1.77 (q, $H_{10,10'}$); IR (KBr) 3450, 3350, 2960, 1740, 1600, 1500, 1260, 1100, 905, 750, 690 cm$^{-1}$.

**General Procedure for Indole Preparation.** The hydrazone or bis(hydrazone) was mixed with polyphosphoric acid (PPA) in a heavy-walled beaker and heated at 100 °C for 1–1.5 h. After cooling, the mixture was made basic with 10% NaOH and extracted with $CH_2Cl_2$ (3 × 75 mL). The combined organic extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to give the indole derivative.

**2-(2′-Pyridyl)indole (1).** The reaction of 2.0 g (9.05 mmol) of 2-acetylpyridine phenylhydrazone with 10 g of PPA provided 1.8 g (97%) of 1 as a yellow solid, mp 145–147 °C (lit.[6] mp 152 °C): $^1$H NMR ($CDCl_3$) $\delta$ 11.91 (bs, NH), 8.35 (d, $H_{6'}$, $J$ = 4.2 Hz), 7.77 (d, $H_{3'}$, $J$ = 8.0 Hz), 7.69, 7.62 (overlapping t, $H_{4'}$, $H_{5'}$), 7.33 (d, $H_7$, $J$ = 8.0 Hz), 7.21–7.06 (m, $H_4$, $H_5$, $H_6$), 7.00 (s, $H_3$); IR (KBr) 3100, 3010, 1580, 1430, 1400, 1330, 1290, 1140, 990, 770, 740 cm$^{-1}$.

**3,3′-Methylene-2-(2′-pyridyl)indole (7a).** The reaction of 0.26 g (1.1 mmol) of hydrazone **6a** with 2.5 g of PPA provided 0.23 g (95%) of **7a** as a white solid, mp 246–250 °C dec; $^1$H NMR[24] ($CDCl_3$) $\delta$ 10.48 (bs, NH), 8.46 (d, $H_{13}$, $J$ = 3.9 Hz), 7.80, 7.68, 7.50 (3 d, $H_3$, $H_6$, $H_{11}$), 7.28–7.12 (m, $H_4$, $H_5$, $H_{12}$), 3.76 (s, $CH_2$); IR (KBr) 3120, 3040, 1570, 1400, 1170, 1085, 765, 710 cm$^{-1}$.

**3,3′-Dimethylene-2-(2′-pyridyl)indole (7b).** The reaction of 1.0 g (4.0 mmol) of hydrazone **6b** with 3.5 g of PPA provided 0.62 g (65%) of **7b** as a thick yellow oil. Crystallization from EtOH–$Et_2O$ gave a yellow solid, mp 108–110 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 11.91 (bs, NH), 8.35 (d, $H_{14}$, $J$ = 4.4 Hz), 7.52, 7.36, 7.18 (3 d, $H_3$, $H_6$, $H_{12}$), 7.12–7.02 (m, $H_{13}$ + 2ArH), 6.93 (t, ArH, $J$ = 5.4 Hz), 2.98 (s, 4 H, $CH_2$); IR (KBr) 3170, 2940, 1600, 1450, 1385, 1345, 1280, 1130, 1000, 780, 720 cm$^{-1}$.

**3,3′-Trimethylene-2-(2′-pyridyl)indole (7c).** The reaction of 0.61 g (2.31 mmol) of hydrazone **6c** with 3.5 g of PPA provided 0.53 g (62%) of **7c** as a yellow solid, mp 215–217 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 10.02 (bs, NH), 8.24 (d, $H_{15}$, $J$ = 4.1 Hz), 7.39 (d, 1 H, $J$ = 7.7 Hz), 7.20 (d, 1 H, $J$ = 7.4 Hz), 7.14 (d, 1 H, $J$ = 8.0 Hz), 7.06 (t, 1 H, $J$ = 7.3 Hz), 6.93 (t, 1 H, $J$ = 7.3 Hz), 6.83 (dd, 1 H, $J$ = 4.9, 6.9 Hz), 2.98 (t, $ArCH_2$), 2.74 (m, $ArCH_2$), 1.93 (m, -$CH_2$-); IR (KBr) 3400, 3020, 2890, 1560, 1440, 1425, 1400, 1310, 1090, 950, 770, 720 cm$^{-1}$.

**3,3′-Tetramethylene-2-(2′-pyridyl)indole (7d).** The reaction of 0.15 g (0.54 mmol) of hydrazone **6d** with 1.5 g of PPA provided 0.083 g (59%) of **7d** as a pale yellow solid, mp 151–153 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 9.32 (bs, NH), 8.37 (d, $H_{16}$, $J$ = 4.3 Hz), 7.45 (d, 1 H, $J$ = 7.8 Hz), 7.39 (d, 1 H, $J$ = 7.5 Hz), 7.19 (d, 1 H, $J$ = 7.9 Hz), 7.11–6.99 (m, 3 H), 2.98 (m, 2 H, $ArCH_2$), 2.81 (m, 2 H, $ArCH_2$), 1.77 (m, 4 H, -$CH_2$-); IR (KBr) 3125, 2880, 1560, 1440, 1415, 1310, 1245, 1085, 780, 725 cm$^{-1}$.

**2,6-Di(2′-indolyl)pyridine.** The reaction of 1.0 g (2.9 mmol) of 2,6-diacetylpyridine bis(phenylhydrazone) with 10 g of PPA provided 0.80 g (89%) of 2,6-di(2′-indolyl)pyridine as a yellow solid, mp 245–247 °C: $^1$H NMR ($CDCl_3$) $\delta$ 9.65 (bs, NH), 7.73 (m, $H_4$), 7.65 (2 overlapping d, 4 H), 7.50 (d, 2 H, $J$ = 8.1 Hz), 7.25 and 7.13 (two t, $H_{5'}$ and $H_{6'}$), 7.07 (s, $H_{3'}$); IR (KBr) 3420, 1600, 1570, 1310, 800, 755 cm$^{-1}$.

**3,3′:5,3″-Bis(dimethylene)-2,6-di(2′-indolyl)pyridine (10a).** The reaction of 0.30 g (0.75 mmol) of bis(hydrazone) **9a** with 5.0 g of PPA provided 0.23 g (84%) of **10a** as a red solid, mp 215–216 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 10.23 (bs, NH), 7.48 (d, $H_6$, $J$ = 7.3 Hz), 7.30 (d, $H_3$, $J$ = 8.0 Hz), 7.25 (s, $H_{12}$), 7.13 and 7.04 (2 t, $H_4$ and $H_5$, $J$ = 7.0, 7.3 Hz), 2.96 (s, 8 H, $H_9$, $H_{10}$), 2.24 (s, NH); IR (KBr) 3070, 2970, 2850, 1670, 1595, 1455, 1435, 1420, 1360, 1165, 750 cm$^{-1}$; exact mass calcd for $C_{25}H_{19}N_3$ $m/e$ 361.15790, found 361.15828.

**3,3′:5,3″-Bis(trimethylene)-2,6-di(2′-indolyl)pyridine (10b).** The reaction of 0.07 g (0.165 mmol) of bis(hydrazone) **9b** with 1.50 g of PPA provided 0.052 g (82%) of **10b** as a yellow solid, mp 120–122 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 9.63 (bs, NH), 7.45 (d, $H_6$, $J$ = 7.7 Hz), 7.22 (d, $H_3$, $J$ = 7.9 Hz), 7.12 (overlapping s and t, 6 H), 7.07 (s, $H_{13}$), 6.99 (t, 4 H, $J$ = 7.3 Hz), 3.01 (m, 4 H, $ArCH_2$), 2.75 (m, 4 H, $ArCH_2$), 2.0 (m, 4 H, -$CH_2$-); IR (KBr) 3400 (b), 2930, 1680, 1560, 1460, 1330, 1260, 745 cm$^{-1}$; exact mass calcd for $C_{27}H_{23}N_3$ $m/e$ 389.1892, found 389.1921.

**3,3′:5,3″-Bis(tetramethylene)-2,6-di(2′-indolyl)pyridine (10c).** The reaction of 0.140 g (0.31 mmol) of bis(hydrazone) **9c** with 2.5 g of PPA provided 0.108 g (84%) of **10c**, mp 219–221 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 8.95 (bs, NH), 7.59 (d, $H_6$, $J$ = 7.8 Hz), 7.41 (s, $H_{14}$), 7.36 (d, $H_3$, $J$ = 8.0 Hz), 7.23–7.10 (overlapping t, $H_4$ and $H_5$), 3.11 (m, 4 H), 2.93 (m, 4 H), 1.85 (m, 8 H), 1.66 (bs, NH); IR (KBr) 3450, 2930, 1450, 1330, 750 cm$^{-1}$; exact mass calcd for $C_{29}H_{27}N_3$ $m/e$ 417.22050, found 417.22075.

**3,3′-Trimethylene-2,2′-biindole (14b).** A solution of 0.175 g (0.575 mmol) of bis(hydrazone) **12b** in 10 mL of acetic acid was refluxed for 6 h. After cooling, 25 mL of $H_2O$ was added and the mixture was extracted with dichloromethane (3 × 25 mL). The organic extracts were dried over $Na_2SO_4$, filtered, and concentrated to give a thick red oil, which was chromatographed on 20 g of silica gel, eluting with dichloromethane to afford two products, **14b** and **13b**.

**14b** ($R_f$ = 0.6), 40 mg (23%), mp 215–218 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 7.94 (bs, NH), 7.52 (d, $H_6$, $J$ = 7.0 Hz), 7.39 (d, $H_3$, $J$ = 8.1 Hz), 7.14 (m, $H_{4,5}$), 3.10 (m, 4 H, $H_{9,11}$), 2.15 (m, $H_{10}$); IR (KBr) 3410, 2930, 1450, 1340, 1110, 905, 745 cm$^{-1}$.[25]

**13b**: ($R_f$ = 0.4), 70 mg (60%), mp 139–141 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 8.93 (bs, NH), 7.67 (d, $H_4$, $J$ = 8.1 Hz), 7.37 (bs, 2H), 7.14 (m, 1 H), 3.17 (dd, $ArCH_2$), 2.86 (dd, $COCH_2$), 2.12 (m, 2 H), 2.03 (m, 2H); IR (KBr) 3320, 2930, 1620, 1540, 1450, 1350, 1260, 1110, 910, 760 cm$^{-1}$. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 7.04. Found: C, 77.91; H, 6.74; N, 6.97.

**3,3′-Tetramethylene-2,2′-biindole (14c).** Following the procedure outlined above for **14b**, the reaction of 0.20 g (0.63 mmol) of bis(hydrazone) **12c** in acetic acid afforded two products after chromatography on silica gel ($CH_2Cl_2$), **14c** and **13c**.

**14c** ($R_f$ = 0.65), 37 mg (21%), mp 78–80 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 7.96 (bs, NH), 7.59 (d, $H_6$, $J$ = 7.6 Hz), 7.38 (d, $H_3$, $J$ = 7.8 Hz), 7.3–7.15 (m, $H_{4,5}$), 3.02 (bs, $H_{9,12}$), 1.92 (bs, $H_{10,11}$); IR (KBr) 3400, 2930, 1460, 1350, 1110, 900, 750 cm$^{-1}$.[25]

**13c** ($R_f$ = 0.5), 80 mg (60%), mp 173–175 °C: $^1$H NMR[24] ($CDCl_3$) 9.1 (bs, NH), 7.69 (d, $H_4$, $J$ = 8.0 Hz), 7.40–7.31 (m, 2 H), 7.14 (t, 1 H), 3.30 (t, $ArCH_2$, $J$ = 6.6 Hz), 3.01 (t, $COCH_2$, $J$ = 7.1 Hz), 1.85–1.75 (2 overlapping m, 4 H), 1.47 (m, 2 H); IR (KBr) 3310, 2930, 1630, 1530, 1450, 1340, 1260, 910, 750 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.58. Found: C, 78.37; H, 6.74; N, 6.97.

**[2,3:7,6]-Bis(2′,3′-indolino)tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane (17).** The reaction of 0.31 g (0.87 mmol) of bis(hydrazone) **16** with

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(24) The NMR atom numbering scheme for the bridged indoles designates the indole nitrogen as atom number one and each carbon atom on the periphery of the molecule is then numbered sequentially in the direction opposite the nearest heteroatom. Atoms identical by symmetry are only designated once.

(25) This biindole was too unstable for satisfactory analysis. Earlier workers noted similar behavior for the dimethylene derivative **14a**.[11a]

3.0 g of PPA provided 0.192 g (68%) of **17**, mp >300 °C: $^1$H NMR ($CDCl_3$) $\delta$ 8.21 (s, NH), 6.89 (overlapping d and t, 4 ArH), 6.51 (t, 2 ArH, $J$ = 7.4 Hz), 6.42 (d, 2 ArH, $J$ = 7.6 Hz), 5.92 (s, NH), 2.63 (bs, 2 H), 2.33 (bs, 2 H), 2.11 (bs, 2 H), 1.50 (dd, $H_{10,10'}$, $J$ = 9.9, 10.7 Hz); IR (KBr) 3380, 2940, 1735, 1610, 1460, 1265, 1100, 810 cm$^{-1}$; exact mass calcd for $C_{23}H_{18}N_2{\cdot}NH_3$ $m/e$ 339.17355, found 339.17364.

**Cyclopalladation of 1.** A suspension of 0.10 g (0.52 mmol) of 2-(2′-pyridyl)indole (**1**) and 0.078 g (0.26 mmol) of palladium 2,4-pentanedionate (Alfa) in 10 mL of methanol was refluxed overnight. The precipitate that formed was collected and washed with hexane to give 89 mg (86%) of a yellow-green solid, mp 208–210 °C, which was identified as **19e** by its spectral properties: $^1$H NMR ($CDCl_3$) $\delta$ 8.26 (d, $H_{6'}$, $J$ = 5.5 Hz), 7.95 (d, 1 H, $J$ = 8.4 Hz), 7.67 (t, $H_{4'}$, $J$ = 7.5 Hz), 7.61 (d, 1 H, $J$ = 7.7 Hz), 7.53 (d, 1 H, $J$ = 7.8 Hz), 7.1–6.9 (m, 3 H), 6.92 (s, $H_3$), 5.51 (s, =CH), 2.21 (s, $CH_3$), 2.10 (s, $CH_3$); IR (KBr) 3060, 1570, 1520, 1450, 1385, 1365, 1320, 1030, 910, 750 cm$^{-1}$. Anal. Calcd for $C_{18}H_{16}N_2O_2Pd$: C, 54.21; H, 4.02; N, 7.03. Found: C, 54.04; H, 4.08; N, 6.95.

**Cyclopalladation of 7a.** Following the procedure outlined above for **19e**, the reaction of 20 mg (0.091 mmol) of 3,3′-methylene-2-(2′-pyridyl)indole (**7a**) with 27 mg (0.091 mmol) of palladium 2,4-pentanedionate afforded 12 mg (32%) of **19a**, mp 260 °C dec: $^1$H NMR[24] ($CDCl_3$) $\delta$ 8.71 (d, $H_{13}$, $J$ = 5.8 Hz), 7.76, 7.51, 7.40 (3 d, $H_3$, $H_6$, $H_{11}$), 6.99 (overlapping, t, 2 H), 6.83 (t, 1 H), 5.17 (s, =CH), 3.45 (AB quartet, $H_{9,9'}$), 1.89 (s, $CH_3$), 1.60 (s, $CH_3$); IR (KBr) 1575, 1520, 1380, 740 cm$^{-1}$. Anal. Calcd for $C_{19}H_{16}N_2O_2Pd$: C, 55.55; H, 3.90; N, 6.82. Found: C, 55.11; H, 3.92; N, 6.71.

**Cyclopalladation of 7b.** Following the procedure outlined above for **19e**, the reaction of 0.14 g (0.59 mmol) of 3,3′-dimethylene-2-(2′-pyridyl)indole (**7b**) with 0.09 g (0.295 mmol) of palladium 2,4-pentanedionate afforded 101 mg (80%) of **19b** as orange needles after recrystallization from MeOH–$CHCl_3$, mp 207–209 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 7.82 (d, $H_{14}$, $J$ = 5.7 Hz), 7.67 (d, $H_{12}$, $J$ = 8.4 Hz), 7.43 (overlapping d, 2 H), 7.06 (t, 1 H), 6.91 (t, 1 H), 6.85 (t, 1 H), 5.50 (s, =CH), 3.14 (s, $CH_2CH_2$), 2.20 (s, $CH_3$), 2.09 (s, $CH_3$); IR (KBr) 3030, 2930, 1555, 1510, 1370, 915, 785, 750 cm$^{-1}$. Anal. Calcd for $C_{20}H_{18}N_2O_2Pd$: C, 56.55; H, 4.24; N, 6.60. Found: C, 56.27; H, 4.31; N, 6.58.

**Cyclopalladation of 7c.** Following the procedure outlined above for **19e**, the reaction of 24 mg (0.10 mmol) of 3,3′-trimethylene-2-(2′-pyridyl)indole (**7c**) with 31 mg (0.10 mmol) of palladium 2,4-pentanedionate afford 33 mg (75%) of **19c**, mp 264–265 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 8.22 (d, $H_{15}$, $J$ = 5.7 Hz), 7.98 (d, 1 H), 7.46 (2 overlapping d, 2 H), 7.09 (t, 1 H), 6.89 (2 overlapping t, 2 H), 5.50 (s, =CH), 3.21 (t, $ArCH_2$), 3.02 (m, $ArCH_2$), 2.20 (s, $CH_3$), 2.13 (m, -$CH_2$-), 2.10 (s, $CH_3$); IR (KBr) 2940, 1570, 1550, 1470, 1385, 745 cm$^{-1}$. Anal. Calcd for $C_{21}H_{20}N_2O_2Pd{\cdot}0.25H_2O$: C, 56.89; H, 4.62; N, 6.32. Found: C, 56.66; H, 4.43; N, 6.27.

**Cyclopalladation of 7d.** Following the procedure outlined for **19e**, the reaction of 23 mg (0.093 mmol) of 3,3′-tetramethylene-2-(2′-pyridyl)indole (**7d**) with 28 mg (0.093 mmol) of palladium 2,4-pentanedionate afforded 41 mg (97%) of **19d**, mp 243–245 °C: $^1$H NMR[24] ($CDCl_3$) $\delta$ 8.27 (d, $H_{16}$, $J$ = 5.8 Hz), 8.00, 7.54, 7.48 (3 d, $H_3$, $H_6$, $H_{14}$), 7.09 (t, 1 H), 7.01 (dd, 1 H), 6.94 (t, 1 H), 5.48 (s, =CH), 3.15 (m, $ArCH_2$), 3.02 (m, $ArCH_2$), 2.18 (s, $CH_3$), 2.08 (s, $CH_3$), 2.04–1.87 (2 overlapping m, -$CH_2CH_2$-); IR (KBr) 2935, 1570, 1520, 1460, 1390, 740 cm$^{-1}$. Anal. Calcd for $C_{22}H_{22}N_2O_2Pd{\cdot}1.25H_2O$: C, 55.58; H, 5.15; N, 5.89. Found: C, 55.24; H, 4.57; N, 5.51.

**Cycloruthenation of 7b.** To a solution of 0.126 g (0.28 mmol) of *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$[26] in 20 mL of absolute EtOH was added 0.066 g (0.28 mmol) of indole **7b**, and the mixture was refluxed for 20 h. After cooling, 0.090 g (0.56 mmol) of $NH_4PF_6$ in 3 mL of $H_2O$ was added and the resulting precipitate was collected to give 0.150 g of crude material, which was chromatographed on alumina, eluting with $CH_3CN$/toluene, 1:3 to 1:1. On standing, the intermediate fraction gave 0.092 g (36%) of $Ru(bpy)_2$(**7b**)$(PF_6)$ as dark red crystals: $^1$H NMR ($CD_3CN$) $\delta$ 8.5–6.9 (complex overlapping m, 23 ArH), 3.04 (m, 4 H, -$CH_2$-); IR (KBr) 3050, 1625, 1445, 1375, 830, 755, 555 cm$^{-1}$; FAB mass spectrum, $m/e$ 776 [$Ru(bpy)_2$(**7b**)$(PF_6)^+$], 631 [$Ru(bpy)_2$(**7b**)$^+$].

**Acknowledgment.** Financial support from the Robert A. Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8607935) is gratefully acknowledged. The NMR spectrometer was partially funded by NSF (CHE-866352). We also thank Professor Gordon Gribble for helpful discussions, Jean-Luc Lim for preparation of diketone **15**, and S. Fink for assistance with the mass spectra.

**Registry No.** **1**, 13228-40-5; **5a**, 31170-78-2; **5b**, 56826-69-8; **5c**, 41043-13-4; **5d**, 97919-78-3; **6a**, 119273-94-8; **6b**, 39585-90-5; **6c**, 119273-95-9; (*Z*)-**6d**, 119273-96-0; (*E*)-**6d**, 119273-97-1; **7a**, 119273-98-2; **7b**, 119273-99-3; $Ru(bpy)_2$(**7b**)$(PF_6)$, 119295-98-6; **7c**, 119274-00-9; **7d**, 119274-01-0; **8a**, 63371-62-0; **8b**, 96413-29-5; **8c**, 96413-30-8; **9a**, 119274-02-1; **9b**, 119274-03-2; **9c**, 119274-04-3; **10a**, 119274-05-4; **10b**, 119274-06-5; **10c**, 119274-07-6; **12b**, 57234-08-9; **12c**, 57234-09-0; **13b**, 7257-25-2; **13c**, 16244-20-5; **14b**, 119274-08-7; **14c**, 119274-09-8; **15**, 25282-60-4; **16**, 119274-10-1; **17**, 119274-11-2; **19a**, 119295-99-7; **19b**, 119296-00-3; **19c**, 119296-01-4; **19d**, 119296-02-5; **19e**, 119296-03-6; *cis*-$Ru(bpy)_2Cl_2$, 19542-80-4; 2-acetylpyridine, 1122-62-9; 2-acetylpyridine phenylhydrazone, 7734-05-6; phenylhydrazine, 100-63-0; 2,6-diacetylpyridine, 1129-30-2; 2,6-diacetylpyridine bis(phenylhydrazone), 3882-42-6; 1,2-cycloheptanedione, 3008-39-7; 1,2-cyclooctanedione, 3008-37-5; 2,6-di(2′-indolyl)pyridine, 3882-41-5; palladium 2,4-pentanedionate, 14024-61-4.

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