could be realized with equal probability. This result is of interest, as two previously proposed[8] structural models of the zinc binding sites in DNA-binding proteins,[9] $Zn(S\text{-}2,4,6\text{-}iPr_3C_6H_2)_2(bpy)$ (**7**) and $Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(Me\text{-}imid)_2$ (**8**), where iPr = *i*-C_3H_7 and Me-imid = *N*-methylimidazole, both contain tetracoordinate Zn(II) in distorted-tetrahedral ligand environments and neither exhibits a tendency to form pentacoordinated adducts with nitrogen bases. The failure of **7** and **8** to form pentacoordinated adducts may be due to the high electron densities on zinc caused by the strong bonding interactions with the powerfully nucleophilic substituted thiophenolato ligands. It should be noted that neither **7** nor **8** formed an adduct with CH_3CN, under the same conditions where a closely related Co(II) complex produced the pentacoordinated 1:1 adduct $Co(S\text{-}2,6\text{-}iPr_2C_6H_3)_2(bpy)(CH_3CN)$ (**9**).[10] Evidently, Co(II) may accommodate another donor ligand because the high electron density on cobalt is offset by the availability of d orbitals for back-bonding. However, with appropriate ligands, even Zn(II) reveals its tendency to form pentacoordinated structures and actually favors pentacoordination over tetracoordination.

This study also indicates that 5 is the maximally attainable coordination number in neutral zinc complexes with sulfur and nitrogen ligands. We believe that this result can be generalized and that it has biological significance inasmuch as it suggests the plausibility of pentacoordinated zinc especially in the functional states zinc proteins and enzymes. Which coordination number is ultimately realized appears to depend primarily on the effective electron density on zinc. While tricoordinated structures may be confirmed to anionic complexes such as exemplified by the recently characterized[4] anion $Zn(SR)_3^-$, in neutral complexes pentacoordination is favored over tetracoordination only at low electron densities on zinc. Depending on the donor strengths of the ligands, limiting cases may result in which pentacoordination is only barely favored over tetracoordination. Such is the case in **5**, where the bpy ligand still permits one of the two sulfur ligands to remain bidentate, although the coordinate $Zn\text{-}S(CH_3)$ bond is quite weak. The other sulfur ligand in **5** is forced to adopt a monodentate coordination in which the $S\text{-}CH_3$ group is in a clearly noninteractive position in the solid state. This arrangement is not necessarily retained in solution, as the free $S(CH_3)$ group could interact dynamically with zinc in solution. This interaction may facilitate the exchange of coordinated bpy with free bpy, as suggested by the variable-temperature ^1H NMR measurements; since Co(II) and other metals may substitute Zn(II) in DNA-binding proteins and enzymes and this heterometallic substitution has been suggested[11] as relevant to the mechanisms of metal toxicity, teratogenicity, or carcinogenicity, similar studies will now be conducted on thiol-thioether complexes of other elements.

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Supplementary Material Available: For complexes **2**, **3**, and **5**, tables of atomic positions, scattering factors, least-squares planes, thermal parameters, bond distances, and bond angles, crystal lattice diagrams, tables and test describing crystallographic details, and a textual presentation of VT NMR data for Figure 4 (42 pages); listings of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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A Bis(terpyridine)ruthenium(II) Catenate

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A new catenate has been synthesized that contains a pseudooctahedral coordination site and a ruthenium(II) center. The compound is built by entwining two functionnalized terpyridine derivatives around the metal prior to cyclizing the system. The yield for the double cyclization step (four phenolate groups of the precursor complex and 2 equiv of the diiodo derivative of hexaethylene glycol) is modest (11%) but allows preparation of several tens of milligrams per experiment. The catenate obtained consists of two interlocked 38-membered rings. The ruthenium(II) catenate is nonluminescent at room temperature in CH_3CN, similar to other bis(terpyridine) complexes. Demetalation of the free catenand has not yet been carried out.

Introduction

In the last few years we have been interested in the synthesis and study of coordinating molecular systems consisting of two or more interlocked rings.[1] Catenanes in general have been discussed in relatively old literature, and various synthetic approaches have been suggested and developed.[2,3]

An efficient synthesis of interlocked rings has recently been developed. It is based on a three-dimensional template synthesis around a transition-metal ion.[4-8] Cu(I) is used to bind two molecules of a 2,9-disubstituted 1,10-phenanthroline: in the tetrahedral complex the two ligands are mutually perpendicular and organized into an arrangement such that cyclization of each phenanthroline fragment leads to two interlocked rings (Scheme I). The resulting copper complex (a *catenate*) is readily demetalated with cyanide to give the free ligand (a *catenand*).

These ligands have a variety of interesting properties. The geometry of the ligand changes considerably between the free and bound forms,[9] an air-stable nickel(I) complex has been prepared,[10]

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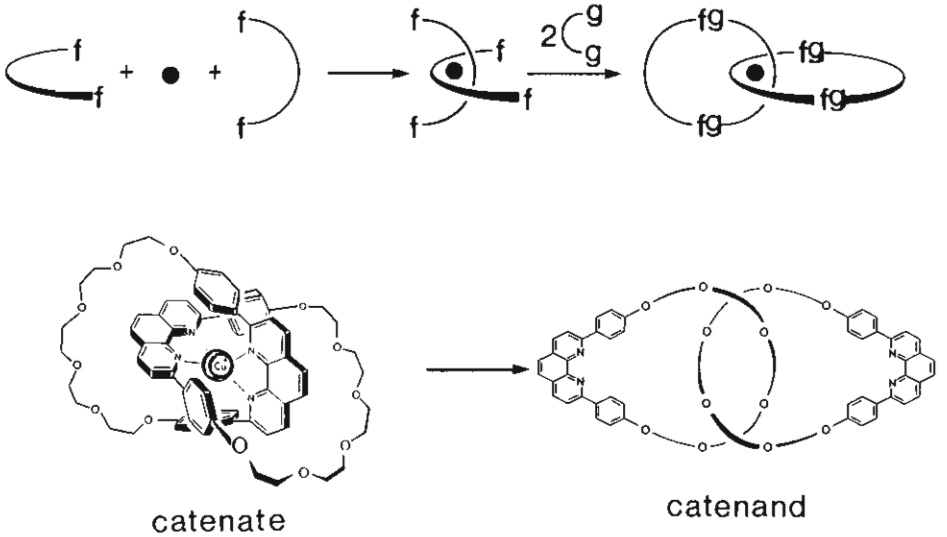
Scheme I. Strategy Used To Prepare Catenates[a]



[a] f and g can form a chemical link; the transition metal (originally copper(I)) is represented by a black circle. A copper(I) *catenate* is quantitatively demetalated to the corresponding *catenand* by CN^-.

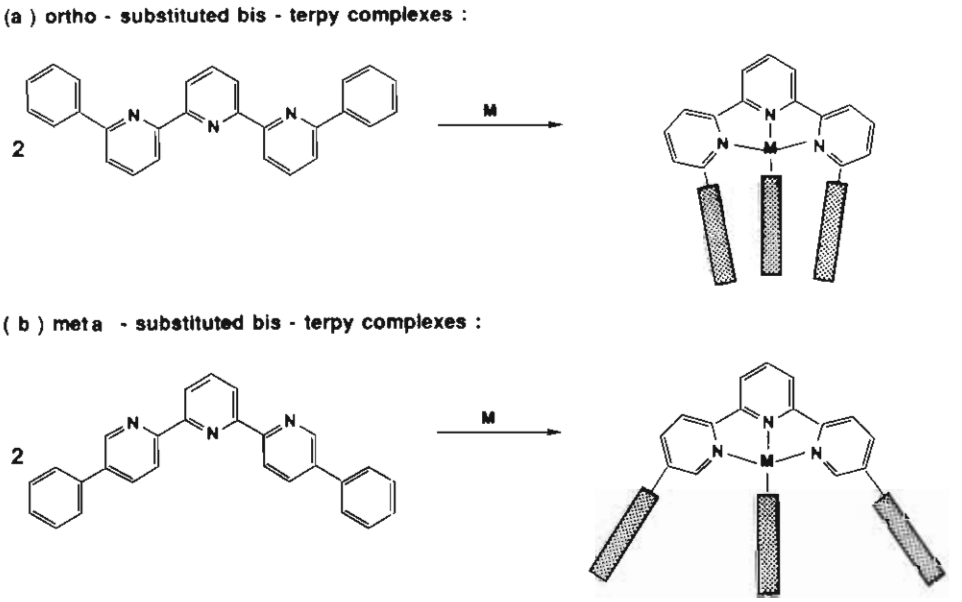


Figure 1. Schematic representation of the reaction leading to a bis(disubstituted terpy) complex. The presence of substituents ortho to the nitrogen atoms causes very severe steric congestion with the second chelating ligand (vertical rectangle) whereas for meta-substituted systems no steric repulsion is expected.

the intertwined topology leads to unexpected physical solution properties,[11] and the Cu(I) complexes have been studied for their photochemical properties.[12] In addition, a Pd(II) complex has been shown to have an interesting and unexpected cyclometalated structure,[13] which arises from a severe mismatch between the steric properties of the ligand binding site (which strongly imposes a tetrahedral geometry on metal ions) and the electronic requirements of the Pd(II) ion (which strongly favor a square-planar geometry). The possibilities for forming low-oxidation-state complexes of second- and third-row transition-metal ions in unusual geometries are extensive and currently under investigation.

To date, however, all of the catenands prepared have been based around macrocycles containing 2,9-diphenyl-1,10-phenanthroline, leading to a tetrahedral binding site for transition-metal ions. This is primarily due to the efficient synthetic procedure that has been developed; the Cu(I) catenate depicted in Scheme I can be prepared in 20% overall yield in just four steps starting from 1,10-phenanthroline.[8] It is perfectly possible to envisage other donor sets in the binding site of new catenands; a good candidate is 2,2′:6′,2″-terpyridine (terpy), with its rich and well-characterized coordination chemistry[14] and the potential use of its Ru(II) complexes in photochemistry.[15] Accordingly, we now wish to report the synthesis of the first catenate containing an octahedral binding site for transition-metal ions, as its Ru(II) complex $[Ru(cat\text{-}38)][PF_6]_2$ (Scheme II), via a three-dimensional template synthesis of two interlocked terpy-containing macrocycles around a ruthenium(II) ion.

Results

The new complex $[Ru(cat\text{-}38)][PF_6]_2$ consists of two interlocked 38-membered macrocyclic rings, each incorporating a 5,5″-di-

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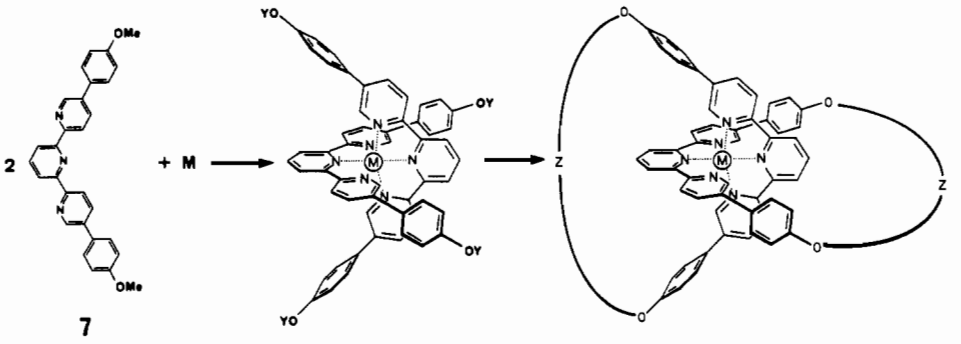
Scheme II. Synthesis of a Bis(terpy) Catenate Following the Strategy Depicted in Scheme I



substituted terpy fragment and a poly(oxyethylene) linker chain. The key step in the synthesis involves reaction of the ruthenium(II) complex of 5,5″-bis(4-hydroxyphenyl)terpyridine (**8**) with 2 equiv of the diiodo derivative of hexaethylene glycol under high-dilution conditions in DMF. The ruthenium(II) ion serves as the template in this case in the same way that copper(I) functions in the syntheses of the phenanthroline-based catenands.

We decided to use the 5,5″-disubstituted terpyridine rather than the more readily accessible 6,6″-disubstituted analogue, since in the latter case the "pinching" of the ligand that arises on coordination to transition-metal ions would cause a very hindered environment around the metal ion (Figure 1). Examination of complexes of 6,6″-diphenylterpyridine with ruthenium(II) showed that this hindered environment results in relatively weakly bound and highly labile complexes.[16,17] In the 5,5″-disubstituted terpy by contrast the substituents do not interfere at all with metal–ligand binding, and moreover, the "pinching" of the ligand on coordination will bring the phenol oxygen atoms closer together into a more suitable arrangement for cyclization (Figure 1).

The intermediate terpyridine **8** is prepared according to the route outlined in Scheme III by a Potts-type synthesis starting from 2-acetyl-5-(4-methoxyphenyl)pyridine (**4**). The first step is a conventional coupling of the Grignard reagent from 4-bromoanisole with 3-bromopyridine, using $Ni(PPh_3)_2Cl_2$ as catalyst. This reaction is based on a published method,[18] with the important variation that the temperature of the highly exothermic reaction is carefully controlled. This results in a yield of 74%, as opposed to the literature yield of 32%. **1** is then converted to its *N*-oxide **2** by the normal method (H_2O_2 in glacial acetic acid)[19] in 75% yield. Subsequent conversion to the cyanide **3** is complicated by the possible formation of two positional isomers. Although the unwanted isomer 2-cyano-3-(4-methoxyphenyl)-pyridine is more sterically hindered than the 2,5-isomer, it is electronically preferred,[20] and attempts to prepare **3** using KCN and benzoyl chloride[19] gave predominantly the 2,3-isomer. The problem is avoided by use of the bulky reagent trimethylsilyl cyanide,[20,21] since steric effects are now much more important than with the small cyanide ion. This gives **3** in 62% yield, with only about 25% of the unwanted isomer being formed; the two can be separated by careful chromatography. **3** is converted to **4** by reaction with methylmagnesium iodide in benzene in 80% yield. Despite the toxicity of benzene, it is much the best solvent for this reaction, since **3** is only sparingly soluble in ether and all attempts to do the reaction in THF resulted rapidly in black mixtures and very low yields of **4**. The usefulness of benzene in Grignard reactions involving nitriles has been mentioned elsewhere.[22]

Scheme III. Synthesis of a terpy Chelating Ligand **7** and Numbering of the Molecules for NMR Spectroscopy

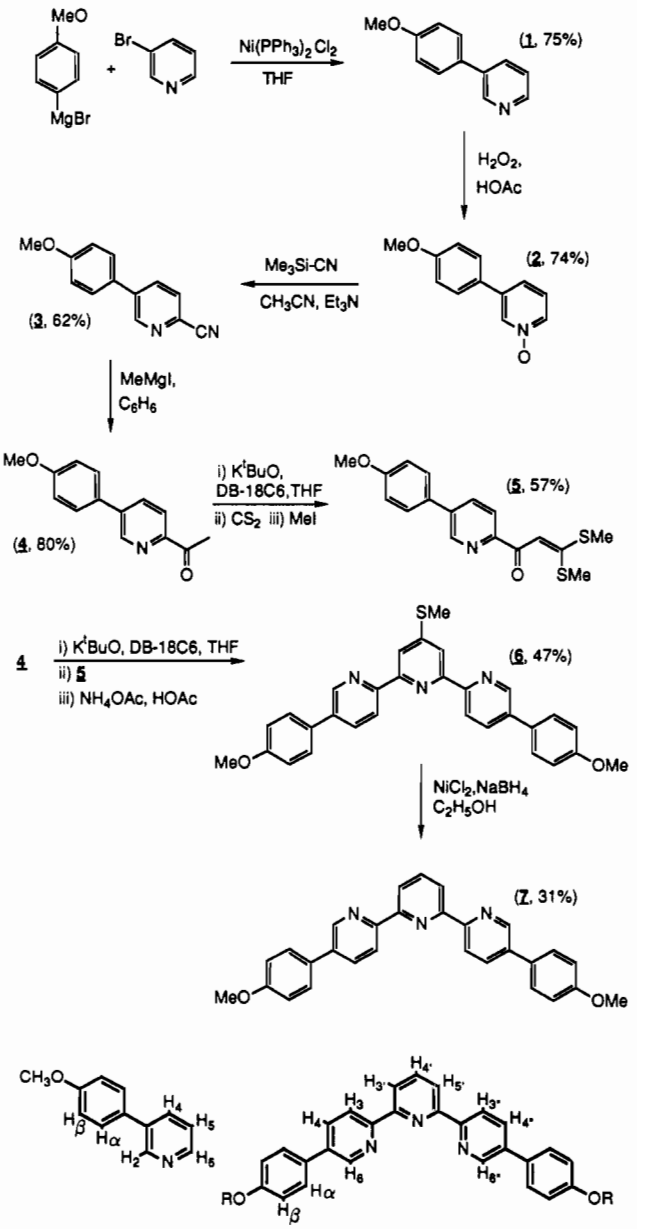


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Table I. Summary of Electrochemical Results

complex	$E_{1/2}[2^+/3^+]^a$ (ΔE_p, mV)	$E_{1/2}[2^+/1^+]$ (ΔE_p, mV)	$E_{1/2}[1^+/0]$ (ΔE_p, mV)
$[Ru(cat\text{-}38)][PF_6]_2$[b]	+1.32 (60)	−1.23 (60)	−1.45 (60)
$[Ru(\mathbf{7})_2][PF_6]_2$[b]	+1.32 (70)	−1.25 (60)	−1.46[c]
$[Ru(terpy)_2][ClO_4]$[d]	+1.25 (60)	−1.40 (60)	−1.65 (80)

[a] All potentials in V vs SCE in acetonitrile. [b] Measured at a scan rate of 200 mV/s. [c] Peak of outward wave; return wave obscured by desorption process. [d] Reference 29.

The three-step Potts method was used[23] to convert **4** to the terpyridine **7**, with one major adaptation. We found it necessary to use dibenzo-18-crown-6 in the first two reactions, both of which use potassium *tert*-butoxide as base. In the first step—preparation of the α-oxo ketene–dithioacetal **5**—only a small amount of the desired product was obtained in the absence of dibenzo-18-crown-6. Instead, significant quantities of the ethyl ketone, isopropyl ketone, and *tert*-butyl ketone were isolated, from repeated reaction of the enolate ion directly with methyl iodide. In the presence of enough dibenzo-18-crown-6 to sequestrate all of the potassium present, a 50% yield of **5** was readily obtained. The second step is reaction of **5** with another 1 equiv of the enolate of **4**; a Michael reaction gives a 1,5-dicarbonyl intermediate, which is ring-closed with ammonium acetate in glacial acetic acid. In the absence of dibenzo-18-crown-6 the yield of **6** is negligible; with it, the yield is 47%. Desulfurization of **6** to give **7** with nickel boride works in only 31% yield, due to the very low solubility of **6** in the conventional solvents for this reaction (methanol, ethanol). An alternative method, using "complex reducing agents" generated from nickel(II) chloride, *tert*-amyl alcohol, and sodium hydride in THF,[24] gave similar yields but with the added complication that **7** is isolated as its nickel(II) complex and requires demetalation with cyanide to liberate the free ligand.

Deprotection of the anisoyl substituents to phenols can be achieved in a variety of ways.[25] In the previous preparations of phenanthroline-based catenands the deprotection is done in molten pyridinium chloride at 210 °C in quantitative yield.[8] In this new preparation, we took advantage of the stability and solubility of the iron(II) and ruthenium(II) complexes of **7** to perform the deprotection *on the metal complex*. This can be achieved very quickly, under mild conditions and in high yield, by using boron tribromide in dichloromethane solution.[26] **7** is readily converted to its iron(II) or ruthenium(II) complexes by reaction with ferrous sulfate in methanol or ruthenium trichloride in ethylene glycol, respectively. As the hexafluorophosphate salts, these complexes are very soluble in dichloromethane, which is an ideal solvent for reactions with boron tribromide. The free ligand **7** by contrast is only sparingly soluble in dichloromethane, and deprotection to **8** with boron tribromide would be further complicated by (a) competing attack of the free basic nitrogen atoms on the reagent and (b) formation of insoluble hydrobromide salts of the ligand during the workup (which liberates HBr). By performance of the deprotection on the complex, all of these problems are avoided.

Finally, the complex $[Ru(\mathbf{8})_2][PF_6]_2$ is cyclized to give $[Ru(cat\text{-}38)][PF_6]_2$ by reaction with the diiodo derivative of hexaethylene glycol (**9**) in the presence of Cs_2CO_3 in DMF under high-dilution conditions. As with the previous syntheses of catenands, the Cs_2CO_3 acts as a convenient deprotonating agent for the phenol functions, the cesium phenolates so obtained being particularly active nucleophilic species.[27]

Table II. Summary of UV–Visible Spectral Data

complex	λ_{max}, nm ($10^{-3}\epsilon$, mol^{-1} L^{-1} cm^{-1})[a]
$[Ru(cat\text{-}38)][PF_6]_2$	475 (19.2), 339 (189), 283 (110), 249 (151)
$[Ru(\mathbf{7})_2][PF_6]_2$	476 (19.2), 336 (170), 281 (103), 249 (90)
$[Ru(terpy)_2]^{2+}$[b]	474 (14.6)
$[Ru(terpy)_2]^{2+}$[c]	470 (16.1), 330 (38), 310 (72.3), 280 (38), 270 (48)

[a] Spectra recorded in acetonitrile apart from $[Ru(terpy)_2]^{2+}$.[c] [b] Reference 15. [c] Reference 30; spectrum recorded in methanol.

$[Ru(cat\text{-}38)][PF_6]_2$ has been characterized by several spectroscopic methods. The FAB mass spectrum shows peaks at m/z = 1573 and 1428 (based on ^{102}Ru), which correspond to $[Ru(cat\text{-}38)][PF_6]^+$ and $[Ru(cat\text{-}38)]^+$, respectively. There is also a peak at m/z = 714 corresponding to the doubly charged ion $[Ru(cat\text{-}38)]^{2+}$, with the same isotopic pattern as the peak at m/z 1428 but with half-integral spacings.

Electrochemical and UV–visible spectroscopic data are summarized in Tables I and II together with the results for $[Ru(\mathbf{7})_2][PF_6]_2$ and $[Ru(terpy)_2]^{2+}$ for comparison purposes.

Discussion

The synthesis of the ruthenium(II) complex $[Ru(cat\text{-}38)]^{2+}$ is a multistep process. The overall yield is only very modest, but the procedure allows preparation of several tens of milligrams per experiment.

The oxidation potentials of the ruthenium(II) ions in the catenate complex and in $[Ru(\mathbf{7})_2][PF_6]_2$ (the open-chain equivalent) are both slightly higher than in $[Ru(terpy)_2]^{2+}$, which is simply an effect of substituting the terpyridine. More important is the fact that the oxidation potentials of $[Ru(cat\text{-}38)][PF_6]_2$ and $[Ru(\mathbf{7})_2][PF_6]_2$ are the same. This indicates that closure of the two macrocyclic rings to form the catenate has not had a large effect on the geometry around the ruthenium ion. It might be expected that if the linker chain were sufficiently short, closure of the rings could pinch the terpyridyl moieties enough to make a noticeable change in the coordination environment of the ruthenium; however, such a change has not been detected. The two ligand-based reductions of $[Ru(cat\text{-}38)][PF_6]_2$ and $[Ru(\mathbf{7})_2][PF_6]_2$ are significantly easier than for $[Ru(terpy)_2]^{2+}$, which would be expected due to the more highly conjugated nature of the ligands: again, however, they are approximately the same.

The UV–visible spectra (see Table II) are consistent with this; the results suggest that the $Ru-N_6$ coordination environment is very similar for all three complexes; therefore, no significant change in the geometry at the metal ion has arisen as a result of closing the macrocyclic rings. The ligand-based $\pi-\pi^*$ transitions for $[Ru(cat\text{-}38)][PF_6]_2$ and $[Ru(\mathbf{7})_2][PF_6]_2$ are somewhat different from those of $[Ru(terpy)_2]^{2+}$, which is to be expected, but they are virtually identical with each other. More importantly, the MLCT transitions (which are sensitive to changes in the metal environment) are virtually identical in all three cases. Preliminary experiments show that $[Ru(\mathbf{8})]^{2+}$ is nonluminescent at room temperature, confirming that the ligand field strength of **8** has not been drastically modified by interlocking as compared to terpy.

Demetalation of the complex to give the free catenand cat-38 is not feasible, due to the very high stability of ruthenium(II) bis(terpyridyl) complexes. Use of iron(II) as the octahedral templating ion would be preferable, since iron(II) bis(terpyridyl) complexes are easily demetalated by oxidation, which precipitates the iron as insoluble iron oxide.[28] Unfortunately attempts to prepare $[Fe(cat\text{-}38)][PF_6]_2$ from $[Fe(\mathbf{8})_2][PF_6]_2$ and the diiodo derivative of hexaethylene glycol failed, precisely because of this tendency of iron(II) bis(terpyridyl) complexes to decompose in basic media. Under the reaction conditions (Cs_2CO_3 in DMF at 65 °C), the intense purple color of the starting complex disappeared in about 2 h, and no identifiable products could be isolated

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from the reaction mixture. Isolation of free cat-38 will require development of an alternative synthetic route that does not require strongly basic conditions for the cyclization step, thus allowing iron(II) to be used as the template.

Experimental Section

General Details. NMR spectra were recorded with a Bruker AM200 spectrometer. UV–visible spectra were recorded with a Uvikon 860 spectrophotometer. Cyclic voltammograms were recorded with a Bruker E130M potentiostat, using a conventional three-electrode configuration (Pt disk working electrode, Pt wire auxiliary electrode, and an SCE reference); the supporting electrolyte was 0.1 M $[^nBu_4N][BF_4]$, recrystallized twice from methanol/water and dried in vacuo at 80 °C. Melting points were measured with a Reichert apparatus and are uncorrected.

THF, ether, and benzene were distilled from dark blue or purple sodium/benzophenone solutions. Acetonitrile and dichloromethane were distilled over calcium hydride. All reagents were of the highest grade of purity available commercially and were used as received. The diiodo derivative of hexaethylene glycol was prepared by a published method.[30]

Preparation of 3-(4-Methoxyphenyl)pyridine (1). In a 1-L, 3-neck flask equipped with a thermometer, argon inlet, and rubber septum cap are placed 3-bromopyridine (34.4 g, 0.21 mol), $Ni(PPh_3)_2Cl_2$ (2.2 g, 3.4 mmol), and THF (500 mL). The flask is flushed with argon and cooled to −10 °C. To this heterogeneous, stirred mixture is added via a double-ended cannula a solution of the Grignard reagent formed from Mg (6.3 g, 0.259 mol) and 4-bromoanisole (48.5 g, 0.259 mol) in THF (200 mL). There is an excess of approximately 25% of the Grignard reagent. After the addition, the cooling is ended and an exothermic reaction begins. The temperature is allowed to rise slowly to 40 °C, at which point vigorous cooling is applied to reduce the reaction temperature to 20 °C. If the reaction temperature is allowed to rise above 40 °C, the rate of heating becomes very rapid: the mixture boils very vigorously and the yield is considerably reduced. The reaction mixture is kept between 20 and 40 °C until no further spontaneous heating occurs and is then stirred for a further 1 h.

The mixture is poured into 200 mL of 2 M aqueous HCl and most of the THF removed on a rotary evaporator. The acidic solution is washed with ether and neutralized. A yellow oil separates, which is extracted with several portions of dichloromethane. The organic extract is dried over $MgSO_4$ and evaporated to dryness to give the product as a pale yellow solid. It retains traces of CH_2Cl_2 tenaciously and is best dried on a vacuum line at about 70 °C (above its melting point). The crude yield is 75%; the product is sufficiently pure for use in the next step. If desired, it can be purified by chromatography on a short silica column with 95% CH_2Cl_2/5% MeOH as eluent.

^{1}H NMR, CD_2Cl_2, δ (ppm): 3.85 (3 H, s, OCH_3), 7.02 (2 H, d, J = 8.8 Hz, 2 H_α), 7.33 (1 H, ddd, J = 7.9, 4.8, 0.8 Hz, H_5), 7.55 (2 H, d, J = 8.8 Hz, 2 H_β), 7.85 (1 H, ddd, J = 7.9, 2.4, 1.7 Hz, H_4), 8.51 (1 H, dd, J = 4.8, 1.7 Hz, H_6), 8.80 (1 H, dd, J = 2.4, 0.8 Hz, H_2). Mp: 54–56 °C (lit.[18] mp 55–57 °C). FABMS: m/z = 185 (M^+).

Preparation of 3-(4-Methoxyphenyl)pyridine *N*-Oxide (2). To a solution of **1** (25 g, 0.135 mol) in glacial acetic acid (250 mL) is added H_2O_2 (20 mL of 30% by volume solution). The mixture is heated to 80 °C for 3 h with stirring. Additional H_2O_2 (20 mL of 30% by volume solution) is added and the solution stirred for a further 3 h, by which time it is a pale orange. About three-quarters of the acetic acid is removed on a rotary evaporator. The remaining acidic slurry is neutralized and extracted with CH_2Cl_2 (several extractions are necessary due to the slight solubility of the *N*-oxide in water). The combined organic extracts are dried over $MgSO_4$, and the solvent is evaporated, giving the *N*-oxide **2** as a pale yellow solid in 74% yield. It is sufficiently pure to use directly in the next step but can be recrystallized from CH_2Cl_2 if desired.

^{1}H NMR, CD_2Cl_2, δ (ppm): 3.85 (3 H, s, OCH_3), 7.02 (2 H, d, J = 8.9 Hz, 2H_α), 7.29 (1 H, t, J = 6.3 Hz, H_5), 7.42 (1 H, d, J = 8.0 Hz, H_4), 7.51 (2 H, d, J = 8.9 Hz, 2 H_β), 8.08 (1 H, d, J = 6.3 Hz, H_6), 8.38 (1 H, s, H_2). FABMS: m/z = 185 (M^+ − O). Mp: 118–121 °C.

Preparation of 2-Cyano-5-(4-methoxyphenyl)pyridine (3). This was prepared by the reaction of the *N*-oxide **2** (20.15 g, 0.101 mol) with trimethylsilyl cyanide (25 g, 0.252 mol, 2.5 equiv) and triethylamine (15.2 g, 0.15 mol) in acetonitrile (250 mL) exactly according to the published method. As well as the desired product, the crude mixture contains some of the unwanted positional isomer 2-cyano-3-(4-methoxyphenyl)pyridine and other minor impurities. The required product is separated by careful chromatography on silica with 98% CH_2Cl_2/2% MeOH: it has an R_f value of about 0.5, with the minor product slightly behind. The yield of pure 2-cyano-5-(4-methoxyphenyl)pyridine is 62%.

^{1}H NMR, CD_2Cl_2, δ (ppm): 3.84 (3 H, s, OCH_3), 7.05 (2 H, d, J = 8.9 Hz, 2 H_α), 7.59 (2 H, d, J = 8.9 Hz, 2 H_β), 7.74 (1 H, dd, J = 8.2, 0.8 Hz, H_5), 7.98 (1 H, dd, J = 8.2, 2.4 Hz, H_4), 8.92 (1 H, dd, J = 2.4, 0.8 Hz, H_2). FABMS: m/z = 210 (M^+). Anal. Found: C, 73.9; H, 4.8; N, 13.3. Calcd for $C_{13}H_{10}N_2O$: C, 74.3; H, 4.8; N, 13.3. Mp: 118–119 °C.

Preparation of 2-Acetyl-5-(4-methoxyphenyl)pyridine (4). In a 500-mL, 3-neck flask fitted with a thermometer, rubber serum cap, and an argon inlet is placed a solution of **3** (6.00 g, 28.6 mmol) in dry benzene (250 mL). The solution, under argon, is cooled in an ice/salt bath; some of the starting material precipitates. To this cold suspension is transferred by a double-ended cannula a solution of MeMgI (1.5 equiv, prepared from Mg (1.18 g, 48.5 mmol) and MeI (6.08 g, 42.8 mmol) in ether (40 mL)), upon which a yellow-green color appears. The cooling bath is removed, and the mixture is left to stir for 3 h, by which time it has reached room temperature. The intermediate ketimine is hydrolyzed by addition of aqueous ammonium chloride with vigorous stirring for 2 min; the yellow-green color disappears. The two layers are separated, and the aqueous layer is further extracted with dichloromethane. The combined organic extracts are dried over $MgSO_4$ and evaporated to dryness to give a crude brown solid. The product is purified by silica column chromatography with 98% CH_2Cl_2/2% MeOH as eluent, to give 2-acetyl-5-(4-methoxyphenyl)pyridine as a white solid in 80% yield.

^{1}H NMR, CD_2Cl_2, δ (ppm): 2.70 (3 H, s, CH_3), 3.86 (3 H, s, OCH_3), 7.04 (2 H, d, J = 8.9 Hz, 2 H_α), 7.62 (2 H, d, J = 8.9 Hz, 2 H_β), 7.96–8.08 (2 H, m, H_4 + H_5), 8.88 (1 H, dd, J = 2.2, 1.0 Hz, H_2). FABMS: m/z = 227 (M^+). Anal. Found: C, 74.3; H, 5.9; N, 6.1. Calcd for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.8; N, 6.2. Mp: 91–92 °C.

Preparation of 5,5″-Bis(4-methoxyphenyl)terpyridine (7). This was prepared from 2-acetyl-5-(4-methoxyphenyl)pyridine (**4**) in three steps. The method of Potts was followed, with the variation that we found it necessary to add dibenzo-18-crown-6 to the first two reaction mixtures to obtain even modest yields.

3,3′-Bis(methylthio)-1-(2-(5-(4-methoxyphenyl))pyridinyl)-2-propen-1-one (5). In an argon-flushed 250-mL, 3-neck flask equipped with a reflux condenser, dropping funnel, and argon inlet are placed THF (100 mL), K^{t}BuO (3.26 g, 29 mmol), and dibenzo-18-crown-6 (10.49 g, 32 mmol). To the stirred suspension is added over 15 min a solution of **4** (3.00 g, 13 mmol) in THF (50 mL); a bright yellow solid (the potassium enolate) precipitates. To this suspension is then added slowly a solution of CS_2 (1.14 g, 15 mmol) in THF (10 mL). The reaction mixture becomes bright orange. After 10 min of stirring, a solution of MeI (4.26 g, 30 mmol) in THF (10 mL) is slowly added, upon which the orange color disappears and the mixture becomes green-brown. The heterogeneous mixture is stirred for 12 h at room temperature and then poured into cold water (200 mL). The suspension is extracted with several portions of CH_2Cl_2, and the combined extracts are dried ($MgSO_4$) and the solvent removed. The bulk of the solid product is dibenzo-18-crown-6 potassium iodide; the desired dithioacetal is separated by chromatography on silica gel with CH_2Cl_2 as eluent. It appears as a dark orange band, just ahead of the dibenzo-18-crown-6 potassium iodide, which appears as a dark brown band. The orange solid is dissolved in CH_2Cl_2, ethanol added, and the CH_2Cl_2 allowed to evaporate to give 3,3-bis(methylthio)-1-(2-(5-(4-methoxyphenyl))pyridinyl)-2-propen-1-one as orange crystals in 50% yield.

^{1}H NMR, $CDCl_3$, δ (ppm): 2.57 (3 H, s, SCH_3), 2.69 (3 H, s, SCH_3), 3.87 (3 H, s, OCH_3), 7.03 (2 H, d, J = 8.4 Hz, 2 H_α), 7.59 (2 H, d, J = 8.4 Hz, 2 H_β), 7.67 (1 H, s, −CH=), 8.03 (1 H, d, J = 8.2 Hz, H_4), 8.25 (1 H, d, J = 8.2 Hz, H_5), 8.86 (1 H, s, H_2). FABMS: m/z = 331 (M^+). Mp: 163–164 °C.

4′-(Methylthio)-5,5″-bis(4-methoxyphenyl)terpyridine (6). In an argon-flushed 250-mL, 3-neck flask equipped with a reflux condenser, argon inlet, and dropping funnel are placed K^{t}BuO (1.96 g, 17.5 mmol), dibenzo-18-crown-6 (6.29 g, 17.5 mmol), and THF (50 mL). To the stirred suspension is added dropwise a solution of **4** (1.94 g, 8.5 mmol) in THF (25 mL) to generate the yellow enolate. Then a solution of the dithioacetal **5** (2.83 g, 8.5 mmol) in THF (50 mL) is added dropwise; a very intense red precipitate appears. This mixture is stirred for 12 h at room temperature and is then treated with ammonium acetate (5 g) and glacial acetic acid (50 mL). The mixture is refluxed for 2 h, the THF removed by distillation, and the resulting dark paste treated with cold water (100 mL), neutralized, and extracted with several portions of CH_2Cl_2. The organic extracts are dried ($MgSO_4$), and the solvent is removed.

The solid mass is suspended in methanol (100 mL) and $FeSO_4 \cdot 7H_2O$ (1 g, excess) added: a deep purple coloration of the iron(II) complex of **6** appears. The mixture is stirred vigorously for 1 h and filtered; the solid filter cake is further extracted with methanolic $FeSO_4 \cdot 7H_2O$ until it does not give a purple coloration with Fe(II). The purple solution so obtained

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is treated with NH_4PF_6 to precipitate the purple complex, which is collected by filtration. The free ligand **6** is obtained in 47% yield by demetalation of the purple solid with H_2O_2/OH^- according to a published procedure,[28] followed by extraction into CH_2Cl_2 and recrystallization from CH_2Cl_2/acetonitrile.

^1H NMR, CD_2Cl_2, δ (ppm): 2.68 (3 H, s, SCH_3), 3.87 (6 H, s, 2 × OCH_3), 7.05 (4 H, d, J = 8.6 Hz, 4 H_α), 7.65 (4 H, d, J = 8.6 Hz, 4 H_β), 8.05 (2 H, dd, J = 7.8, 2.2 Hz, $H_{4,4''}$), 8.36 (2 H, s, $H_{3',5'}$), 8.68 (2 H, d, J = 8.3 Hz, $H_{3,3'}$), 8.91 (2 H, d, J = 2.2 Hz, $H_{6,6''}$). FABMS: m/z = 491 (M^+). Anal. Found: C, 73.8; H, 5.1; N, 8.1. Calcd for $C_{30}H_{25}N_3O_2S$: C, 73.3; H, 5.1; N, 8.6. Mp: 187–189 °C.

5,5''-Bis(4-methoxyphenyl)terpyridine (7). This is prepared from **6** by reduction with nickel boride in ethanol exactly according to the Potts method. After the reaction is complete, the dark reaction mixture is filtered through Celite. The solid mass is extracted with several portions of boiling toluene, each time being filtered hot through Celite. The combined toluene extracts are cooled and reduced in volume, and a white solid is collected by filtration. It is washed with a little cold CH_2Cl_2 to remove any unreacted starting material. Yield of **7**: 31%.

^1H NMR, CD_2Cl_2, δ (ppm): 3.89 (6 H, s, 2 × OCH_3), 7.07 (4 H, d, J = 8.4 Hz, 4 H_α), 7.67 (4 H, d, J = 8.4 Hz, 4 H_β), 7.99 (1 H, t, J = 8.0 Hz, $H_{4'}$), 8.08 (2 H, dd, J = 8.4, 2.1 Hz, $H_{4,4''}$), 8.50 (2 H, d, J = 7.7 Hz, $H_{3',5'}$), 8.71 (2 H, d, J = 7.8 Hz, $H_{3,3''}$), 8.93 (2 H, d, J = 2.1 Hz, $H_{6,6'}$). FABMS: m/z = 445 (M^+). Anal. Found: C, 78.2; H, 5.2; N, 9.4. Calcd for $C_{29}H_{23}N_3O_2$: C, 78.2; H, 5.2; N, 9.4. Mp: 278–280 °C.

Preparation of $Ru(7)_2(PF_6)_2$. A mixture of **7** (150 mg, 0.34 mmol) and $RuCl_3 \cdot 3H_2O$ (50 mg, 0.19 mmol, 0.56 equiv) in ethylene glycol (20 mL) is heated to 160 °C for 12 h. After cooling, the orange solution is filtered, treated with aqueous NH_4PF_6, and extracted into CH_2Cl_2. The solvent is removed in vacuo and the solid residue recrystallized from CH_2Cl_2/MeOH to give $Ru(7)_2(PF_6)_2$ in 81% yield.

^1H NMR, DMSO, δ (ppm): 3.74 (3 H, s, OCH_3), 6.95 (4 H, d, J = 8.8 Hz, 4 H_α), 7.35 (4 H, d, J = 8.8 Hz, 4 H_β), 7.47 (2 H, d, J = 1.4 Hz, $H_{6,6'}$), 8.29 (2 H, dd, J = 8.6, 1.7 Hz, $H_{4,4''}$), 8.55 (1 H, t, J = 8.0 Hz, $H_{4'}$), 8.83 (2 H, d, J = 8.6 Hz, $H_{3,3''}$), 9.08 (2 H, d, J = 8.1 Hz, $H_{3',5'}$). FABMS: m/z = 1137, 992, and 496 (based on ^{102}Ru), corresponding to $[Ru(7)_2][PF_6]^+$, $[Ru(7)^2]^+$, and the doubly charged $[Ru(7)_2]^{2+}$ (the latter peak having half-integral spacings).

Preparation of 5,5''-Bis(4-hydroxyphenyl)terpyridine (8) as Its Ru(II) Complex. To a stirred solution of $Ru(7)_2(PF_6)_2$ in CH_2Cl_2 at −78 °C under argon is added BBr_3 (8 equiv, 2-fold excess). A precipitate immediately forms. The cooling is ended and the mixture allowed to attain room temperature. The reaction is quenched with water and filtered, and the solid product is washed with acetonitrile until the washings are colorless. The yield of $Ru(8)_2(PF_6)_2$ is 90%; it can be recrystallized from DMF or methanol.

^1H NMR, DMSO, δ (ppm): 6.77 (8 H, d J = 8.2 Hz, 8 H_α), 7.25 (8 H, d, J = 8.2 Hz, 8 H_β), 7.43 (4 H, d, J = 2.0 Hz, $H_{6,6''}$), 8.24 (4 H, dd, J = 8.3, 2.0 Hz, $H_{4,4''}$), 8.55 (2 H, t, J = 8.0 Hz, $H_{4'}$), 8.84 (4 H, d, J = 8.3 Hz, $H_{3,3''}$), 9.08 (4 H, d, J = 8.0 Hz, $H_{3',5'}$), 9.92 (2.6 H, s, 4 × OH; integral low due to exchange with H_2O in solvent and disappears on D_2O shake). FABMS: m/z = 935 and 519 (based on ^{102}Ru), corresponding to $[Ru(8)(8 - H^+)]^+$ and $[Ru(8)]^+$, respectively. Some small peaks at higher mass were observed due to formation of adducts with the supporting matrix. Anal. Found: C, 53.2; H, 3.6; N, 7.3. Calcd for $[Ru(C_{27}H_{19}N_3O_2)_2][PF_6]_2 \cdot C_3H_7NO$: C, 52.7; H, 3.5; N, 7.6.

Preparation of $[Ru(cat\text{-}38)][PF_6]_2$. In a 1-L, 3-neck flask equipped with an efficient magnetic stirrer, thermometer, high-dilution addition funnel, and argon inlet is placed degassed DMF (250 mL) and anhydrous Cs_2CO_3 (4 g). The stirred suspension is warmed to 60 °C and maintained at this temperature and under argon throughout the reaction. To this suspension is added dropwise a solution of $[Ru(8)_2][PF_6]_2$ (360 mg, 0.294 mmol) and the diiodo derivative of hexaethylene glycol (360 mh, 0.717 mmol, 2.4 equiv) in degassed DMF (250 mL) over 12 h, and then the mixture is stirred for a further 12 h. A further portion of the diiodo derivative of hexaethylene glycol (70 mg, 0.139 mmol) in degassed DMF (100 mL) is then added dropwise to the reaction mixture over 4 h, and the mixture is allowed to stir for a further 12 h.

The solvent is removed under reduced pressure (complete removal of DMF is essential, since the presence of trace amounts considerably complicates the subsequent chromatography). The brown solid residue is extracted thoroughly with CH_2Cl_2 and the orange extract concentrated to about 20 mL. To this is added a solution of NH_4PF_6 (1 g) in water (10 mL), and the mixture is stirred vigorously overnight to effect complete anion exchange. Separation of the organic layer, drying ($MgSO_4$), and removal of the solvent yields an orange solid, which is chromatographed on silica with CH_2Cl_2/MeOH (95:5). Any excess of the diiodo derivative of hexaethylene glycol and its decomposition products elute first; the desired product appears as an intense orange band, which can be separated completely from the polymeric material remaining on the column. The yield of $[Ru(cat\text{-}38)][PF_6]_2$ is 55 mg, 11%. The complex is recrystallized from dichloromethane/ether.

^1H NMR, $CDCl_3$, δ (ppm): 3.2–4.4 (48 H, m, aliphatic protons in poly(oxyethylene)chain), 7.04 (8 H, d, J = 8.9 Hz, 8 H_α), 7.14 (8 H, d, J = 8.9 Hz, 8 H_β), 7.35 (4 H, d, J = 1.8 Hz, $H_{6,6''}$), 8.10 (4 H, dd, J = 8.5, 1.8 Hz, $H_{4,4''}$), 8.64 (2 H, t, J = 8.2 Hz, $H_{4'}$), 9.00 (4 H, d, J = 8.5 Hz, $H_{3,3''}$), 9.29 (4 H, d, J = 8.2 Hz, $H_{3',5'}$). FABMS: m/z = 1573, 1428, 714 (based on ^{102}Ru), corresponding to $[Ru(cat\text{-}38)][PF_6]^+$, $[Ru(cat\text{-}38)]^+$, and the doubly charged $[Ru(cat\text{-}38)]^{2+}$ (the latter peak having half-integral spacings). Anal. Found: C, 54.0; H, 5.0; N, 5.1. Calcd for $[Ru(C_{78}H_{82}N_6O_{14})][PF_6]_2$: C, 54.5; H, 4.8; N, 4.9.

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Registry No. **1**, 5958-02-1; **2**, 135943-39-4; **3**, 135943-40-7; **4**, 135943-41-8; **5**, 135943-42-9; **6**, 135943-43-0; **7**, 135943-44-1; **8**, 135943-45-2; **9**, 118798-05-3; $[Ru(7)_2][PF_6]_2$, 135943-47-4; $[Ru(8)_2][PF_6]_2$, 135943-49-6; $[Ru(cat\text{-}38)][PF_6]_2$, 135943-51-0; $Ni(PPh_3)_2Cl_2$, 14264-16-5; (*p*-methoxyphenyl)magnesium bromide, 13139-86-1; 3-bromopyridine, 626-55-1.