111. Synthesis and Metal-Binding Properties of Polybipyridine Ligands Derived from Acyclic and Macrocyclic Polyamines

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Synthetic procedures have been developed for the preparation of ligands bearing two to six pendent, unsubstituted or substituted 2,2′-bipyridine groups attached to acyclic (tripode, tetrapode) and macrocyclic (triazanonadecane, cyclam, hexacyclen, bis(bipyrido)hexaazamacrocycle) polyamines. Ligands **1**–**5** have been obtained in high yield by condensation of 6-(bromomethyl)-2,2′-bipyridine (**9b**) with the corresponding amines in the presence of NaOH, H_2O, and MeOH. Ligands **6**–**8** have been prepared in good yield by condensation of **9b** or the di- or tetrasubstituted mono(bromomethyl)bipyridine **10b** or **11b**, respectively, with the corresponding amines in the presence of Na_2CO_3 and MeCN. Ligand **1** forms hemi-cage complexes with Ru^{II}, Fe^{II}, Cr^{II}, and Cr^{III} cations and trinuclear complexes with $[RuCl_2(bpy)_2]$ and $[ReCl(CO)_5]$. Tetrapode **2** and hexapode **4** gave tetranuclear and dinuclear complexes, respectively, by reaction with Fe^{II} salts. These complexes possess a variety of interesting physical and chemical properties.

Introduction. – The coordination chemistry of 2,2′-bipyridine (bpy) ligands has received considerable interest in the past two decades [1]. The properties of the long-lived, luminescent, metal-to-ligand-charge-transfer state, characteristic of polypyridine transition-metal complexes, enable these compounds to sensitize photoinduced electron-transfer and energy-transfer processes [2–4]. These attractive features prompted the introduction of the bpy subunit into macrocyclic [5–9] and macrobicyclic structures [6] [10–14], thus, yielding ligands capable of forming photoactive metal-cage complexes. In particular, inclusion complexes of lanthanides [15–17] and ruthenium(II) [18] [19] have been shown to combine the features of polycyclic structures with the properties associated with bpy groups. Less rigid (*e.g.* acyclic or branched) polydentade complexing agents allow binding properties and structural flexibility to be combined and are well adapted for the synthesis of hemi-caged metal complexes. Moreover, these kinds of ligands are suitable for the preparation of polymetallic complexes which are of interest for their potential multiredox and catalytic properties. One could also envisage that caged or hemi-caged metal ions would prevent ligand photodissociation, hence increasing both excited-state life-times and luminescence quantum yields [18] [20].

Pyridine tripode-type ligands, such as tris[(pyrid-2-yl)methyl]amine, were first synthesized twenty years ago [21], and the stability constants of their numerous first-row-transition-metal complexes have been determined [22]. Analogous polypode ligands [23–27] have been prepared and their copper(II) [25] [28], copper(I) [23] [24] [26], and iron(III) [27] complexes isolated; some examples include α,α′-bis{*N*,*N*-bis-[2-(pyrid-2-yl)ethyl]-amino}-*o*-, -*m*-, or -*p*-xylene [23] [24], tris[2-(pyrid-2-yl)ethyl]amine [25], bis[2-(pyrid-2-yl)ethyl]amine connected by alkyl chains of varying lengths [26], and tetrakis(picolyl)diamine joined together by a C_3 or C_4 chain [27]. Polyazamacrocycles functionalized

with one, three, or four pendent pyridine side arms have also received widespread attention, *e.g.*: 6-[2-(pyrid-2-yl)ethyl]-1,4,8,11-tetraazacyclotetradecane [29], 3,11-dibenzyl-7-[(pyrid-2-yl)methyl]-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene [30], 5-(pyrid-2-yl)-1,4,8,11-tetraazacyclotetradecane [31], tris[(pyrid-2-yl)methyl]-1,4,7-triazacyclononane [32], tris[(pyrid-2-yl)methyl]-1,5,9-triazacyclododecane [32], and 1,4,8,11-tetrakis[(pyrid-2-yl)methyl]-1,4,8,11-tetraazacyclotetradecane [33].

More recently, the synthesis of tri- and tetraazamacrocycles with a single pendent coordinating bipyridinyl group and their complexation properties have also been reported [34] [35].

Polybipyridine tripode-type ligands have been synthesized earlier, incorporating an N-atom [36], a 1,3,5-trisubstituted benzene [11] [14] [37], or a triazamacrocycle (this work) as anchoring unities for the bpy ligands. We describe here a detailed study of our work on the synthesis and some complexation properties of polybipyridine ligands **1–8** derived from acyclic and macrocyclic polyamines. Preliminary results of this work have been previously published [36].

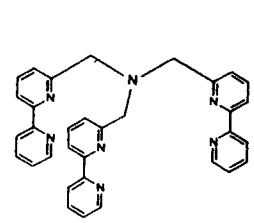
Ligands 1–5. – Reaction of 6-(bromomethyl)-2,2′-bipyridine (**9b**) [38] with acylic primary amines (6-(aminomethyl)-2,2′-bipyridine and ethylenediamine) or with polyazamacrocycles (cyclam, hexacyclen, and 1,4,7-triazacyclononane) afforded ligands **1–5** (80% yield for **1** and **2**, 75% for **3**, 40% for **4**, 64% for **5**). In a typical experiment, 6-(aminomethyl)-2,2′-bipyridine[1]) (**9c**; 1 equiv.) and NaOH (2 equiv.) were dissolved in H_2O/MeOH 1:1 and dropwise added to a MeOH solution of **9b** (2 equiv.) at room temperature. Compound **1** was recovered by filtration as pure material. During the synthesis of ligand **4**, 6-(methoxymethyl)-2,2′-bipyridine (**9d**) was obtained as a by-product (see *Exper. Part*).

Ligands 6–8. – Due to the low solubility of both the di- or tetrasubstituted mono(bromomethyl)bipyridines **10b** and **11b** in MeOH and the primary amine **11d** or the secondary macrocyclic diamine **12** in H_2O, the synthetic procedure described above could not be used; hence the following method was developed. Dropwise addition of a MeCN solution containing 2 equiv. of 6-(bromomethyl)-2,2′-bipyridine (**9b**) or 2 equiv. of 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**10b**) [10] to a solution of macrocycle **12** [5] in MeCN at reflux in the presence of Na_2CO_3 yielded, after chromatography (see *Exper. Part*), the branched macrocycles **6** and **7** (70% yield), respectively. A low yield (< 5%) of compound **6** was obtained when Et_3N was used as base instead of Na_2CO_3.

A similar procedure was used for the synthesis of the hexa(*tert*-butyl)ester tripode **8** (76% yield) using 2 equiv. of di(*tert*-butyl) 6-(bromomethyl)-6′-methyl-2,2′-bipyridine-4,4′-dicarboxylate (**11b**) and 1 equiv. of di(*tert*-butyl) 6-(aminomethyl)-6′-methyl-2,2′-bipyridine-4,4′-dicarboxylate (**11d**) as starting materials.

Complexation Properties of Ligand 1 with Ruthenium(II) and Rhenium(I). – It was of interest to us to study the complexation of Ru^{II} and Re^{I} since previous studies had shown that $[(Ru(bpy)_3]^{2+}$ [40] and/or $[ReCl(bpy)(CO)_3]$ [41] catalyzed the photochemical reduction of CO_2. Loss of ligand might limit the use of these kinds of complexes in photocatalysis [40], and it was, thus, hoped that such decomplexation processes might be minimized

[1]) The 6-(aminomethyl)-2,2′-bipyridine (**9c**) was prepared from 6-(bromomethyl)-2,2′-bipyridine (**9b**) and hexamethylenetetramine followed by hydrolysis in conc. HCl solution [39].



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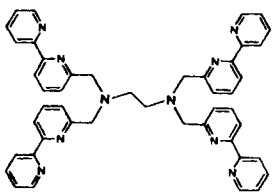

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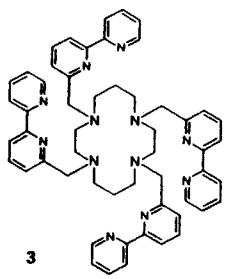

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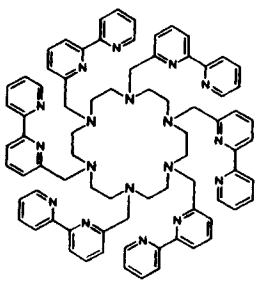

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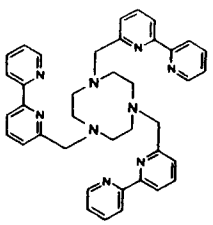

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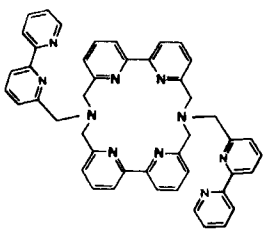

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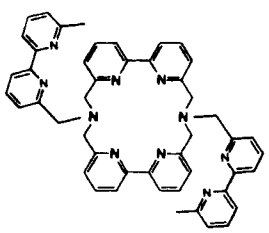

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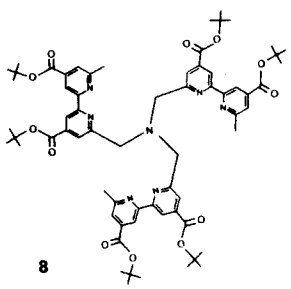

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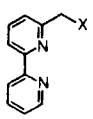
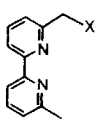


9a X = H
b X = Br
c X = NH_2
d X = OCH_3



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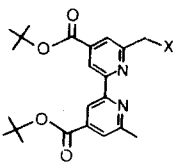
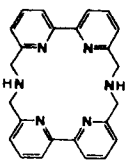
b X = Br



11a X = H
b X = Br
c X = N_3
d X = NH_2



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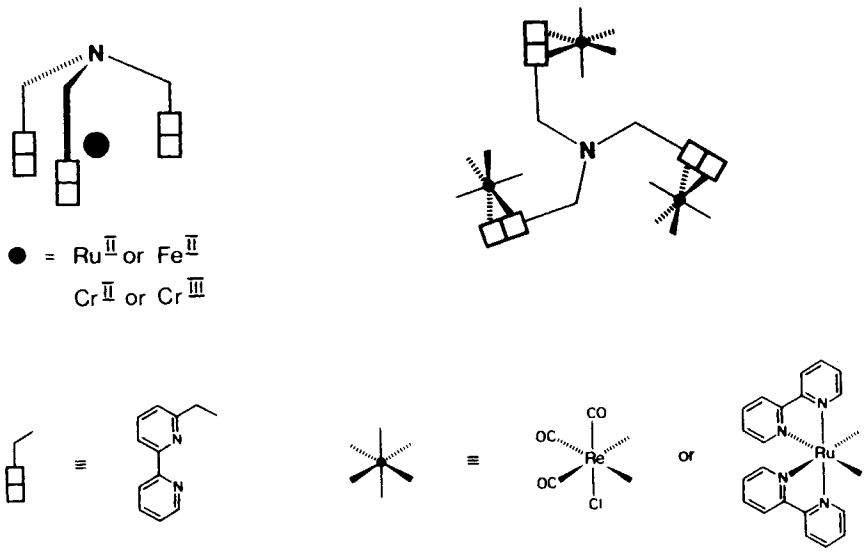
by the use of tripode-like bipyridine ligands. Depending on the nature of the metallic precursor, mononuclear or trinuclear ruthenium(II) complexes **13a** or **14a**, respectively, could be prepared. Stoichiometric reaction of tripode **1** with the so-called 'blue chlororuthenate(II) solution' [42] [43], obtained by hydrogenation of $RuCl_3 \cdot 3H_2O$ in MeOH in the presence of catalytic amounts of platinum black, gave, after workup, the hemi-caged complex $[Ru(\mathbf{1})][PF_6]_2$ (**13a**) (55% yield). The use of $RuCl_3 \cdot 3H_2O$ (a more



13a Ru^{II}, $2[PF_6]^-$
b Fe^{II}, SO_4^{2-}
c Cr^{II}, $2ClO_4^-$
d Cr^{III}, $3ClO_4^-$

14a Ru^{II}
b Re^{I}

$[Fe(\mathbf{4})](ClO_4)_2$ **15**

$[Fe_2(\mathbf{4})](SO_4)_2$ **16**

$[Fe_4(\mathbf{2})_3](SO_4)_4$ **17**

classical synthetic procedure for complexation with 2,2′-bipyridine or 1,10-phenanthroline [44]) gave less than 5% yield of the desired **13a.** This is probably due to the presence of the oxidizable apical N-atom of ligand **1.** Unidentified polymeric complexes were obtained using $[RuCl_2(DMSO)_4]$ [45] as ruthenium source. Similar results were obtained recently during attempts to complexe Ru^{II} with podands based on 1,4,5,8-tetraazaphenanthrene [46].

The ^{1}H-NMR spectra of ligand **1** and of its ruthenium(II) complex $[Ru(\mathbf{1})][PF_6]_2$ (**13a**) were markedly different (see the *Fig.*). The resonance of the aromatic bipyridine protons are shifted downfield upon complexation, as expected. However, the most significant changes occur for H–C(6′) (*o* to the chelating N-atom) and the CH_2 signals. H–C(6′) is shifted upfield by more than 1.5 ppm. This strong shielding (also previously observed[2])) is due to octahedral complexation which forces the proton *o* to the chelating N-atom to lie above the plane of another bpy ligand. The CH_2 signal, a *s* in the free ligand, splits into an *AB* pattern ($J \approx 17$ Hz) upon Ru complexation. Thus, the CH_2 protons have become nonequivalent in the complex pointing to a chiral structure of C_3 symmetry, with helical twisting around the N,Ru axis and slow interconversion (for such distortion in macrobicyclic tris-bpy cryptates, see [10a] [10b]). Furthermore, the very low upfield shift (< 0.1

[2]) For a recent discussion on the ^{1}H-NMR consequences of this configuration, see *e.g.* [47].

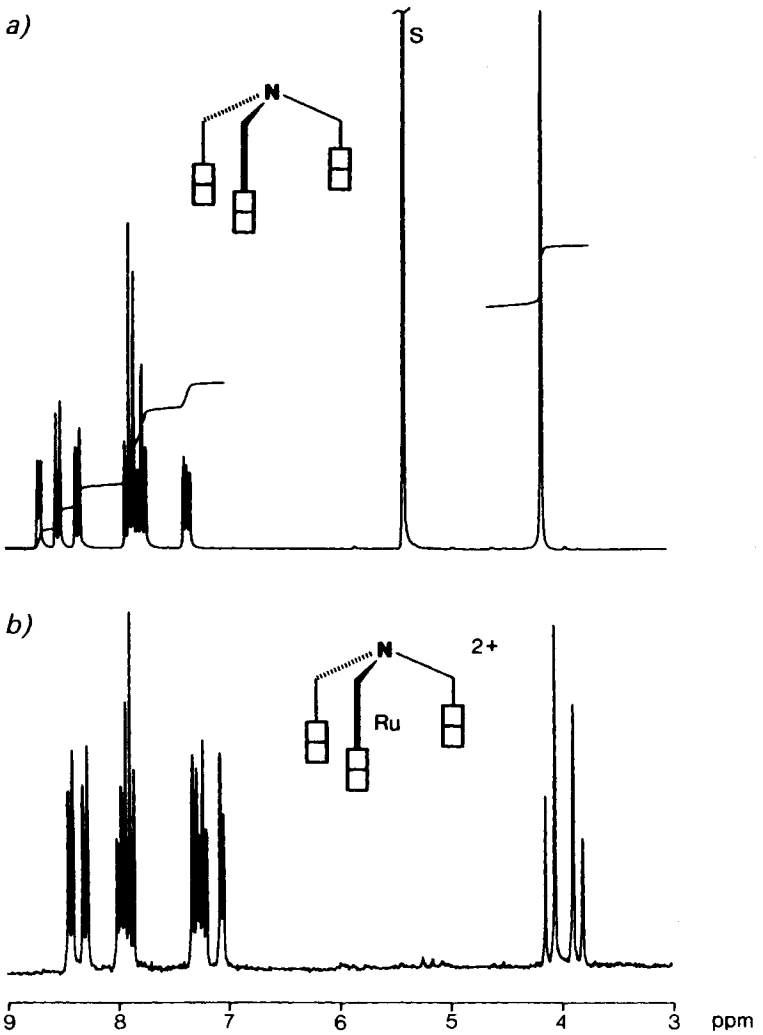


Figure. *200-MHz ^{1}H-NMR spectrum of* a) *ligand* **1** (in CD_2Cl_2) *and* b) *of complex* **13a** (in CD_3CN; solvent signal not shown)

ppm) indicates that they do not lie in the shielding region of the bipyridine units. Only a weak complexation effect was observed on aromatic and aliphatic proton relaxation times (see *Exper. Part*).

Reaction of tripode **1** with 3 equiv. of $[RuCl_2(bpy)_2]\cdot 2H_2O$ [48] in MeOH gave, after workup, the trinuclear complex $[\{Ru(bpy)_2\}_3(\mathbf{1})][PF_6]_6$ (**14a**; 65% yield). Similar reaction of **1** with 3 equiv. of $[ReCl(CO)_5]$ [41] [49] in hot toluene yielded quantitatively the trinuclear complex $[\{ReCl(CO)_3\}_3(\mathbf{1})]$ (**14b**) which has characteristic carbonyl vibrations ($\tilde{\nu}$(CO) 2020, 1915, 1890 cm^{-1}). Both trinuclear complexes **14a** and **14b** were isolated as a mixture of stereoisomers.

Complexation Properties of Tripode 1 with Iron(II), Chromium(II), and Chromium(III). – (Tris-bipyridine)iron and -chromium complexes have already been used to catalyze thermal H_2O oxidation [50] and photochemical H_2O reduction [51], respectively. In both cases, instability of the complexes due to ligand loss was observed; it was hoped that the corresponding hemi-caged iron or chromium complexes would be more stable in this respect. The Fe^{II}-tripode species was synthesized by analogy with the synthesis of $[Fe(bpy)_3]^{2+}$ [52]. Reaction of tripode **1** with $FeSO_4 \cdot 7H_2O$ gave, after workup, the red complex $[Fe(\mathbf{1})]SO_4$ (**13b**; 90% yield) the fast-atom-bombardment (FAB) MS (positive mode) of which exhibits a molecular peak at *m/z* 674. Similarly, the Cr^{II}- and Cr^{III}-tripode complexes were prepared by analogy to the synthesis of $[Cr(bpy)_3]^{2+}$ or $^{3+}$ [53]. Reaction of tripode **1** with $CrCl_2$ gave, after workup, deep-violet, air-sensitive $[Cr(\mathbf{1})](ClO_4)_2$ (**13c**; 88% yield) which after oxidation (O_2) afforded green $[Cr(\mathbf{1})](ClO_4)_3$ (**13d**; 93% yield) whose FAB-MS (positive mode) exhibits a molecular peak at *m/z* 771.

Complexation Properties of Tripode 5, Hexapode 4, and Tetrapode 2 with Iron(II). – Reaction of tripode **5** with $FeSO_4 \cdot 7H_2O$, under the same conditions as above, resulted in the immediate characteristic deep-red coloration (λ_{max} 516 nm) of a tris(bpy)iron species. Due to the instability of the complex, observed by the decrease and finally the loss of the absorption band at 516 nm and formation in solution of iron-hydroxide aggregates, attempts to isolate the pure iron-tripode failed. The difference in behaviour of tripodes **5** and **1** might be explained by the fact that tripode **5** is much more sterically constrained against octahedral complexation of the three bpy arms around the Fe^{II} cation than tripode **1**.

Depending on the stoichiometry of the reaction, mono- or dinuclear iron(II) complexes were isolated. The FAB-MS (positive mode) of the mononuclear iron(II) complex **15** exhibits a molecular peak at 1422 corresponding to $[[Fe(\mathbf{4})]ClO_4]^+$ and a fragmentation peak at 1324 corresponding to loss of ClO_4^- followed by protonation. The FAB-MS (positive mode) of the dinuclear iron(II) complex **16** exhibits a molecular peak at 1571.4 corresponding to $[[Fe_2(\mathbf{4})](SO_4)_2+H^+]$.

Reaction of 3 equiv. of tetrapode **2** with 4 equiv. of $FeSO_4 \cdot 7H_2O$ gave, after workup, deep red $[Fe_4(\mathbf{2})_3](SO_4)_4$ (**17**; 93% yield). All these new polynuclear Fe^{II} complexes were isolated as a mixture of stereoisomers.

Properties of the Ru^{II}, Fe^{II}, Cr^{II}, Cr^{III}, and Re^{I} Complexes. – The results of electronic charge transfer absorption studies, cyclic voltammetry, and coulometry of the complexes are reported in the *Table*.

Electrochemical Studies. Cyclic voltammetry experiments show that the two trinuclear Ru and Re complexes **14a** and **14b** have redox potentials close to those reported for $[Ru(bpy)_3]^{2+}$ and $[ReCl(bpy)(CO)_3]$, respectively. Coulometric oxidation of the trinuclear Ru complex is trielectronic (involving 2.9 e at + 1.45 V *vs.* SCE) and coulometric reduction of the trinuclear Re complex **14b** is trielectronic (involving 2.85 e at – 1.53 V *vs.* SCE). This behaviour can be explained by the fact that the three metal centers in the trinuclear complexes are, as expected, without interactions and, thus, these complexes undergo reversible trielectronic exchange.

The hemi-caged Ru, Fe, and Cr species show interesting properties. $[Ru(\mathbf{1})]^{2+}$ complex **13a** is *ca.* 600 mV easier to oxidize than its $[Ru(bpy)_3]^{2+}$ analogue, but its reduction potentials are close to those of the trinuclear species. The strong effect observed with Ru

Table. *Electronic Charge Transfer Absorption Spectra and Redox Potentials of Complexes* **13a–d**, **14a–b**, *and* **15–17**

Compound	Coordination entity	λ_{max}/nm	(ε_{max})[a]	$E_{1/2}$/V[b])(ΔE/mV[c]))
13a	$[Ru(\mathbf{1})]^{2+}$	462	(9600)	+0.64 (70)
				−1.24 (60)
				−1.42 (60)
				+1.69 (70)
13b	$[Fe(\mathbf{1})]^{2+}$	502	(1150)	+0.76 (60)
				−1.29 (70)
13c	$[Cr(\mathbf{1})]^{2+}$	475	(1770)	−0.39 (70)
				−0.91 (70)
		551	(1750)	−1.37 (70)
13d	$[Cr(\mathbf{1})]^{3+}$	640	(140)	−0.39 (70)
				−0.91 (70)
				−1.37 (70)
14a	$[\{Ru(bpy)_2\}_3(\mathbf{1})]^{6+}$	446	(33000)	+1.36 (90)
				−1.20 (90)
				−1.41 (80)
				−1.68 (80)
14b	$[\{ReCl(CO)_3\}_3(\mathbf{1})]$	360	(6490)	+1.37[d])
				−1.44 (70)
15	$[Fe(\mathbf{4})]^{2+}$	572.5	(4650)	+0.98 (100)
				−1.30 (100)
16	$[Fe_2(\mathbf{4})]^{4+}$	559	(9500)	+0.99 (80)
				−1.24 (100)
17	$[Fe_4(\mathbf{2})_3]^{8+}$	560	(20400)	+0.95 (75)
				−1.32 (85)
	$[Ru(bpy)_3]^{2+}$ [54]	452	(14600)	+1.21 (70)
				−1.23 (70)
				−1.42 (75)
				−1.64 (70)
	$[Fe(bpy)_3]^{2+}$ [55]	520	(8050)	+0.96 (80)
	$[Cr(bpy)_3]^{2+}$ [56] [58]	463	(4150)	−0.31 (80)
		562	(4850)	−080 (80)
				−1.38 (80)
	$[Cr(bpy)_3]^{3+}$ [56] [58]	455	(260)	−0.31 (80)
				−0.80 (80)
				−1.38 (80)
	$[ReCl(bpy)(CO)_3]$ [57]	385	(3100)	+1.30[d])
				−1.37 (70)

[a]) Measured in MeCN for the Ru, Cr, Re, and Fe(**15**) complexes and in H_2O for the other Fe species.

[b]) Obtained from cyclic voltammetry studies on platinum (2 mm^2) or glassy carbon (3.5 mm^2) in dry MeCN containing 0.1M $K[PF_6]$ as supporting electrolyte. Solutions were *ca.* $1 \cdot 10^{-3}$ M in complex, and measurements were made at room temperature under Ar, at 0.4 Vs^{-1} scan rate, with reference to ferrocene as internal standard (quotation relative to the saturated calomel reference electrode).

[c]) The separation between anodic and cathodic peak potentials ΔE_p for ferrocene, under the same conditions, was 70 mV. No compensation was made for internal cell resistance.

[d]) Irreversible metal-localized oxidation.

is weaker with the corresponding Fe and Cr complexes **13b** and **13c** in which the III/II oxidation potential is lower by 200 and 80 mV, respectively.

It is of interest to note that $[Fe(\mathbf{1})]^{2+}$ presents a reversible monoelectronic reduction wave, whereas no reversible reduction could be detected under the same conditions for its $[Fe(bpy)_3]^{2+}$ analogue (see the *Table*). The constrained tris(bipyridinyl)-tripode ligand **1**,

thus, produces appreciable stabilization of the low oxidation states of its complexes with respect to those of the corresponding tris(bpy) complexes, this stabilization being clearly diminished with weak oxidants such as Cr^{III}. This effect is probably due to the participation of the apical N-atom in coordination to the metal, as confirmed by the N···Fe distance in the crystal structure of the Fe^{II} complex [58]. This marked stabilization has not been observed when Fe^{II} or Ru^{II} are complexed by a tris(bpy)-tripode-type ligand containing a neopentylic, C-atom [59][3]) or a 1,3,5-trisubstituted benzene [37], respectively, as anchoring units.

The tris(bpy)-tripode ligand **1** allows the preparation of $[Fe(\mathbf{1})]^+$ by coulometric reduction (0.98 e at -1.38 V *vs.* SCE), the corresponding species is not obtainable with $[Fe(bpy)_3]^{2+}$ complex. With the hexapode and tetrapode ligands **4** and **2**, respectively, the same Fe^I formation effects are observed, but no stabilization of the Fe^{III} species is evidenced on comparison with the free bpy analogues (see complexes **15**–**17** in the *Table*). These results seem to indicate a lack of iron coordination to the non-aromatic N-atoms. Almost no electronic effect is observed when a second Fe^{II} cation is coordinated to the mononuclear hexakis(bpy) species (see complexes **15** and **16** in the *Table*). Coulometric oxidation of complexes **15**, **16**, and **17** are mono-electronic (involving 0.9 e at $+1.07$ V), dielectronic (involving 2 e at $+1.08$ V) and tetraelectronic (involving 3.8 e at $+1.04$ V), respectively, which compares well with tripode complex **13b** (involving 1 e at $+0.85$ V). This confirms the stoichiometry of these complexes and suggests that all metal centers are independent, as observed above for the Ru^{II} and Re^I trinuclear complexes.

Absorption and Fluorescence Studies. The electronic absorption spectra, measured in MeCN for the Cr, Ru, and Re complexes and in H_2O for the Fe species, compare well with the corresponding $[M(bpy)_3]^{2+}$ (M = Ru [54], Fe [55], Cr [56]) and $[ReCl(bpy)(CO)_3]$ [57] analogues (see the *Table*). The trinuclear complexes are fluorescent in MeCN solution at room temperature when excited in their metal-to-ligand charge-transfer absorption bands: $[\{Ru(bpy)_2\}_3(\mathbf{1})]^{6+}$, λ_{em} 610 nm; $[\{ReCl(CO)_3\}_3(\mathbf{1})]$, λ_{em} 598 nm. These values compare well with the ones of the corresponding $[Ru(bpy)_3]^{2+}$ (λ_{em} 607 nm) [54] and $[ReCl(bpy)(CO)_3]$ (λ_{em} 595 nm) [57] analogues. However, no luminescence is detected for the mononuclear tripode complex $[Ru(\mathbf{1})]^{2+}$ at room temperature in various solvent. Steric hindrance at the ruthenium center [61], distortion of the coordination octahedron [4] as well as a rapid internal quenching by the electron pair of the apical N-atom might explain the lack of luminescence.

The results described here provide an efficient access to a novel series of ligands bearing two to six pendent, unsubstituted or substituted 2,2′-bipyridine groups attached to acyclic and macrocyclic polyamines. The tripode-type ligand **1** presents the interesting properties of forming hemi-cage complexes with Ru^{II}, Fe^{II}, Cr^{II}, and Cr^{III} cations and trinuclear complexes with $[RuCl_2(bpy)_2]$ and $[ReCl(CO)_3]$. Work is being pursued to explore further the complexation properties of these ligands, especially with lanthanides, and to use the polynuclear complexes in catalysis, *e.g.* in multielectronic H_2O oxidation or CO_2 reduction.

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[3]) The ligand 5,5″,5‴-[2,2′,2″-ethylidynetris(ethyl)]-5′,5‴,5⁗-trimethyltris[2,2′-bipyridine] ($CH_3C(CH_2CH_2$-bpy-$CH_3)_3$) has been prepared in low yield (*ca.* 5%) by reaction of the monocarbanion of 5,5′-dimethyl-2,2′-bipyridine [60] with 1,1,1-tris(bromomethyl)ethane [59]. Its complex was synthesized as described for **13b**.

Experimental Part

1. *General.* M.p.: uncorrected; *Thomas-Hoover apparatus.* UV/VIS spectra: *Cary-219* spectrophotometer; in MeCN, CH_2Cl_2, or H_2O; molar extinction coefficients from absorbance measurements on at least two different concentrations of complex. IR spectra: *Perkin-Elmer-597* spectrometer; KBr pellets or in soln. with KBr cells.

NMR spectra: at r.t. unless otherwise noted; *Bruker-SY-200* (200.1 (^{1}H) or 50.3 MHz (^{13}C)) or *Bruker-SY-400* spectrometer (400.135 (^{1}H) or 100.654 MHz (^{13}C)); δ(H) in ppm rel. to residual protiated solvent in $CDCl_3$ (7.25), CD_2Cl_2 (5.32), CD_3CN (1.93) and (D_6) acetone (2.05 ppm); δ(C) in ppm rel. to the solvent $CDCl_3$ (77.0), CD_2Cl_2 (53.8), CD_3CN (117.2), or $(CD_3)_6CO$ (205.1 ppm). MS: electronic impact (EI) or chemical ionization (CI) on *LKB-9000S* apparatus; fast-atom bombardment (FAB, positive mode *ZAB-HF-VG-Analytical* apparatus in a *p*-nitrobenzyl alcool (NBA) or monothioglycerol (thio.) matrix unless otherwise specified. Elemental analyses were performed by the Institut de Chimie, Strasbourg, analytical service. Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup comprising a potentiostat, a pilot scanner, a current-potential converter *(EDT-ECP 133)*, and an *xy* recorder *(IFELEC IF3802)*. The working electrode was a platinum rotating disk electrode (*SOLEA Tacussel EDI* type, area 3.14 mm^2) used without rotation for cyclic voltammetry. The reference elctrode (saturated calomel electrode = SCE) was connected to the electrolysis cell by a bridge filled with the same solvent and supporting electrolyte as the soln.

2. *Materials.* 2,2′-Bipyridine *(Fluka)*, ethylenediamine *(Prolabo)*, cyclam *(Aldrich)*, hexacyclen-trisulfate *(Aldrich)*, *N*-bromosuccinimide (NBS; *Fluka*), hexamethylenetetramine *(Fluka)*, dibenzoyl peroxide *(Jannsen)*, $RuCl_3 \cdot 3H_2O$ *(Roth)*, $FeSO_4 \cdot 7H_2O$ *(Prolabo)*, $[Re_2(CO)_{10}]$ *(Aldrich)*, CrCl2 *(Merck)*, and NaN_3 *(Prolabo)* are commercially available.

3. *General Procedure for the Synthesis of* **1**–**5**. To a soln. of **9b** (1g scale, 2*n* equiv.) in MeOH (10 ml) at r.t., a soln. of **9c** or another amine (*n* equiv.) in basic (NaOH, 2*n* equiv.) H_2O/MeOH 1:1 (10 ml) was added dropwise (*ca.* 1 h). After *ca.* 2 h, a white precipitate formed, and the suspension was vigorously stirred at r.t. until the pH approached neutrality (*ca.* 15 h). The white solid was filtered off, washed with H_2O (3 × 10 ml) and Et_2O (3 × 25 ml), and dried under high vacuum. The product was recrystallized in a CH_2Cl_2, hexane, or pentane soln. Filtration and drying afforded pure **1**–**5**. TLC (alumina, 2% MeOH/CH_2Cl_2): single spot.

6-(Bromomethyl)-2,2′-bipyridine [38] (**9b**) was prepared by a procedure adapted from the method described for 6,6′-Bis(bromomethyl)-2,2′-bipyridine [10]: A mixture of **9a** [62] (3.5 g, 20.6 mmol), NBS (4.0 g, 22.5 mmol), and dibenzoyl peroxide (0.25 g) was refluxed in CCl_4 (150 ml) for 6 h. The mixture was cooled to r.t., the succinimide filtered off, and the solvant evaporated. The residue was separated by flash chromatography (silica gel, CH_2Cl_2): **9b** (1.5 g, 30%; R_f 0.12) and 6-(dibromomethyl)-2,2′-bipyridine (1.7 g, 25%, R_f 0.28). **9b**: ^{1}H-NMR (CD_2Cl_2): 8.65 (*dm*, *J* = 4.0, 1 H); 8.45 (*dt*, *J* = 7.8, 1.0, 1 H); 8.35 (*dd*, *J* = 7.8, 0.9, 1 H); 7.83 (*t*, *J* = 7.8, 1 H); 7.82 (*J* = 7.8, 1 H); 7.45 (*dd*, *J* = 7.7, 0.9, 1 H); 7.32 (*ddd*, *J* = 7.8, 4.0, 0.9, 1 H); 4.64 (*s*, 2 H). EI-MS: 250 (100, M^+), 169 (60). *6-(Dibromomethyl)-2,2′-bipyridine:* ^{1}H-NMR (CD_2Cl_2): 8.68 (*d*, *J* = 4.8, 1 H); 8.46 (*d*, *J* = 8.0, 1 H); 8.37 (*dd*, *J* = 8.0, 0.9, 1 H); 7.84 (10-line *m*, 3 H); 7.32 (*ddd*, *J* = 8.0, 4.8, 0.9, 1 H); 6.75 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 158.33; 149.12; 138.59; 137.15; 124.14; 121.93; 121.52; 121.42; 41.90. EI-MS: 326, 328, 330 (100, M^+), 247 ([M − Br]$^+$), 168 ([M − 2 Br]$^+$). Anal. calc. for $C_{11}H_8Br_2N_2$: C 40.27, H 2.46, N 8.54; found: C 40.17, H 2.36, N 8.39.

6-(Aminomethyl)-2,2′-bipyridine (**9c**) was prepared by a procedure adapted from the synthesis of 2-bromoallylamine [39]: To a soln. of hexamethylenetetramine (0.62 g, 4.41 mmol) in CH_2Cl_2 (10 ml) heated at reflux, a soln. of **9b** (1 g, 4.01 mmol) in CH_2Cl_2 (10 ml) was added dropwise and refluxed for further 3 h. The deposited white solid (1.3 g, 84%) was filtered off, dried, and suspended in EtOH (20 ml)/conc. HCl (3 ml). The mixture was stirred at 80° until the solid had completely dissolved (20 h). The soln. was cooled to r.t. and evaporated. H_2O (10 ml) and CH_2Cl_2 (25 ml) were added to the residue, and the mixture was basified (pH *ca.* 13) with conc. NaOH soln. The aq. phase was extracted with CH_2Cl_2 (3 × 25 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. The residue was dissolved in MeOH (20 ml) sat. with HCl (gaz), and **9c** · 3HCl crystallized on addition of Et_2O and standing overnight at 4° (885 mg, 75%). ^{1}H-NMR (D_2O, *t*-BuOH): 8.96 (*d*, *J* = 7.9, 1 H); 8.80 (br. *d*, 2 H); 8.42 (*d*, *J* = 7.9, 1 H); 8.26 (*d*, *J* = 7.9, 1 H); 8.20 (*m*, 1 H); 7.78 (*d*, *J* = 7.8, 1 H); 4.61 (*s*, 2 H). Anal. calc. for $C_{11}H_{11}N_3 \cdot 3HCl$: C 44.84, H 4.79, N 14.26; found: C 44.03, H 4.35, N 14.16.

Tris[(2,2′-bipyridin-6-yl)methyl]amine (**1**). From **9b** (1.02 g, 4.09 mmol) and **9c** (0.38 g, 2.05 mmol.) Recrystallization in CH_2Cl_2/hexane: 860 mg (80%). M.p. 141–142°. ^{1}H-NMR (CD_2Cl_2): 8.63 (*dm*, *J* = 4.8, 0.9, 3 H, H–C(6′)); 8.46 (*d*, *J* = 7.9, 3 H, H–C(3′)); 8.28 (*d*, *J* = 7.8, 3 H, H–C(3)); 7.82 (*t*, *J* = 7.7, 3 H, H–C(4)); 7.78 (*t*, *J* = 7.8, 3 H, H–C(4′)); 7.68 (*d*, *J* = 7.7, 3 H, H–C(5)); 7.29 (*ddd*, *J* = 7.7, 4.9, 0.9, 3 H, H–C(5′)); 4.08 (*s*, 6 H, CH_2); proton relaxation time in s: T_1 5.15 (H–C(6′)); 3.69 (H–C(3′)); 4.18 (H–C(3)); 2.10 (H–C(4)); 2.52 (H–C(4′)); 1.82 (H–C(5)); 2.85 (H–C(5′)); 0.49 (CH_2). ^{13}C-NMR ($CDCl_3$, TMS): 159.17, 156.44, 155.45 (3 *C*C); 149.10, 137.23, 136.77, 123.52, 122.93, 121.23, 119.26 (7 CH); 60.34 (CH_2). EI-MS: 521 (100, M^+), 352 (35,

[$M - CH_2$–bpy]$^+$), 260.5, 176. Anal. calc. for $C_{33}H_{27}N_7$: C 76.00, H 5.18, N 18.81; found: C 75.84, H 5.38, N 18.70.

N,N,N′,N′-Tetrakis[(2,2′-bipyridin-6-yl)methyl]ethylenediamine (**2**). From **9b** (1.2 g, 4.8 mmol) and ethylenediamine (0.072 g, 1.2 mmol). Recrystallization in CH_2Cl_2/hexane: 700 mg (80%). M.p. 138–139°. ^{1}H-NMR (CD_2Cl_2): 8.62 (*dm*, J = 4.8, 1.0, 4 H); 8.38 (*dt*, J = 8.0, 1.0, 4 H); 8.22 (*dd*, J = 7.7, 1.0, 4 H); 7.73 (*td*, J = 7.5, 1.8, 4 H); 7.68 (*t*, J = 7.7, 4 H); 7.5 (*dd*, J = 7.7, 1.0, 4 H); 7.26 (*ddd*, J = 7.6, 4.8, 1.0, 4 H); 3.95 (*s*, 8 H, CH_2–bpy); 2.95 (*s*, 4 H, CH_2N). ^{13}C-NMR ($CDCl_3$, TMS): 159.46, 156.40, 155.38 (3 *C*C); 149.11, 137.19, 136.60, 123.52, 122.82, 121.16, 119.17 (7 CH of bpy); 60.67 (CH_2–bpy), 52.54 (CH_2N). EI-MS: 733 (100, M^+), 565 (60, [$M - CH_2$–bpy]$^+$), 366. Anal. calc. for $C_{46}H_{40}N_{10}$: C 75.41, H 5.46, N 19.13; found: C 75.42, H 5.36, N, 19.02.

1,4,8,11-Tetrakis[(2,2′-bipyridin-6-yl)methyl]-1,4,8,11-tetraazacyclotetradecane (**3**). From **9b** (1 g, 4.0 mmol) and 1,4,8,11-tetraazacyclotetradecane (= cyclam; 0.2 g, 1 mmol). Recrystallization in CH_2Cl_2/pentane; 585 mg (75%). M.p. 105–106°. ^{1}H-NMR (CD_2Cl_2): 8.62 (*dm*, J = 4.8, 1.0, 4 H); 8.37 (*d*, J = 7.9, 4 H); 8.20 (*d*, J = 7.7, 4 H); 7.75 (*td*, J = 7.6, 1.8, 4 H); 7.67 (*t*, J = 7.7, 4 H); 7.51 (*dd*, J = 7.7, 1.8, 4 H); 7.26 (*ddd*, J = 7.6, 4.8, 1.0, 4 H); 3.73 (*s*, 8 H, CH_2–bpy); 2.78 (*s*, 8 H, CH_2N); 2.79 (*t*, J = 6.8, 8 H, CH_2N); 1.87 (*q*, J = 7.3, 4 H, CH_2N). ^{13}C-NMR ($CDCl_3$): 159.92, 156.38, 155.10 (3 *C*C); 149.05, 136.99, 136.74, 123.42, 122.87, 121.08, 119.00 (7 CH of bpy); 61.15 (CH_2–bpy); 51.82, 51.17 (CH_2N); 24.19. EI-MS: 873 (100, M^+), 703 (20, [$M - CH_2$–bpy]$^+$). Anal. calc. for $C_{54}H_{56}N_{12}$: C 74.28, H 6.47, N 19.25; found: C 74.32, H 6.69, N 19.12.

1,4,7,10,13,16-Hexakis[(2,2′-bipyridin-6-yl)methyl]-1,4,7,10,13,16-hexaazacyclooctadecane (**4**). From **9b** (1.2 g, 4.76 mmol) and 1,4,7,10,13,16-hexaazacyclooctadecane (= hexacyclen; 0.205 g, 0.793 mmol). Recrystallization in CH_2Cl_2/pentane: 400 mg (40% from macrocycle). ^{1}H-NMR (CD_2Cl_2): 8.59 (*d*, J = 4.0, 6 H); 8.30 (*d*, J = 8.0, 6 H); 8.16 (*d*, J = 7.2, 6 H); 7.68 (*td*, J = 7.7, 1.8, 6 H); 7.60 (*t*, J = 8, 6 H); 7.37 (*d*, J = 7.2, 6 H); 7.22 (*ddd*, J = 7.7, 4.0, 1.8, 6 H); 3.79, (*s*, 12 H, CH_2–bpy); 2.85 (*s*, 24 H, CH_2N); proton relaxation time in s: T_1 1.26 (H–C(6′)); 2.50 (H–C(3′)); 2.64 (H–C(3)); 2.32 (H–C(4)); 2.55 (H–C(4′)); 2.99 (H–C(5)); 3.15 (H–C(5′)). ^{13}C-NMR ($CDCl_3$): 159.52, 156.25, 155.13 (3 *C*C); 149.02, 137.10, 136.76, 123.45, 122.70, 121.09, 119.07 (7 CH of bpy); 61.16 (CH_2–bpy); 52.93 (CH_2N). EI-MS: 1266 (100, M^+), 1097 (60, [$M - CH_2$–bpy]$^+$), 928 (10, [$M - 2\,CH_2$–bpy]$^+$). Anal. calc. for $C_{78}H_{78}N_{18}$: C 73.91, H 6.20, N 19.89; found: C 73.79, H 6.18, N 19.68.

The mother liquor was evaporated and the residue chromatographed on a silica-gel column (2% MeOH/CH_2Cl_2, yielding) *6-(methoxymethyl)-2,2′-bipyridine* (**9d**) as a colourless liquid (295 mg, 31% from **9b**). R_f 0.43. ^{1}H-NMR (CD_2Cl_2): 8.66 (*dm*, J = 4.8, 0.8, 1 H); 8.45 (*d*, J = 8.0, 1 H); 8.35 (*d*, J = 7.5, 1 H); 7.80 (12-line *m*, 2 H); 7.37 (*d*, J = 7.7, 1 H); 8.28 (8-line *m*, 1 H); 4.65 (*s*, 2 H); 3.49 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 157.84; 148.93; 137.29; 136.67; 124.05; 123.46; 121.47; 121.04; 119.53; 75.52; 58.59. EI-MS: 200 (100, M^+), 169 (10, [$M - OCH_3$]$^+$). Anal. calc. for $C_{12}H_{12}N_2O$; C 71.98, H 6.04, N 13.99; found: C 71.82, H 6.33, N 13.89.

1,4,7-Tris[(2,2′-bipyridin-6-yl)methyl]-1,4,7-triazacyclononane (**5**). From **9b** (0.58 g, 2.3 mmol) and 1,4,7-triazacyclononane [63] (0.1 g, 0.77 mmol). Recrystallization in hot hexane: 310 mg (64%). M.p. 90–91°. ^{1}H-NMR ($CDCl_3$): 8.67 (*d*, J = 4.1, 1 H); 8.40 (*d*, J = 7.9, 1 H); 8.24 (*d*, J = 7.7, 1 H); 7.78 (*t*, J = 7.7, 2 H); 7.55 (*d*, J = 7.7, 1 H); 7.32 (*m*, 1 H); 3.96 (*s*, 2 H); 3.00 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 160.12; 156.39; 155.19; 149.05; 137.08; 136.79; 123.46; 123.10; 121.14; 119.02; 64.78; 55.96. FAB-MS (positive mode): 634.4 (75, [$M + H$]$^+$), 466.3 (8, [$M + H - CH_2$–bpy]$^+$). Anal. calc. for $C_{39}H_{39}N_9$: C 73.90, H 6.20, N 19.89; found: C 73.89, H 6.20, N 19.69.

4. *8,21-Bis[(2,2′-bipyridin-6-yl)methyl]-8,21,27,28,29,30-hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene* (**6**). To a mixture of macrocycle **12** [20] (170 mg, 0.43 mmol) and Na_2CO_3 (1.45 g, 13.68 mmol) in MeCN/CH_2Cl_2 3:1 (40 ml) heated at reflux, a soln. of **9b** (215 mg, 0.86 mmol) in CH_2Cl_2 (10 ml) was added dropwise over 1 h. The mixture was refluxed for further 15 h. After cooling to r.t., the insoluble solid was filtered off, the filtrate evaporated, and the residue chromatographed (silica gel, 5–20% MeOH/CH_2Cl_2), giving **6** as main product (220 mg, 70%). M.p. > 260°. ^{1}H-NMR (DCl/D_2O/*t*-BuOH): 8.83–7.95 (16-line *m*, 26 H); 5.95–5.23 (*m*, 12 H). ^{13}C-NMR (DCl/D_2O/*t*-BuOH): 158.56; 157.79; 155.79; 155.46; 154.52; 148.09; 138.51; 136.71; 136.59; 125.00; 124.08; 123.08; 119.80; 119.54; 118.01; 57.83; 55.29. FAB-MS (positive mode): 731.4 (75, [$M + H$]$^+$), 563.3 (20, [$M + 2\,H - CH_2$–bpy]$^+$), 393.2 (8, [$M + H - 2\,CH_2$–bpy]$^+$). Anal. calc. for $C_{46}H_{38}N_{10}$: C 75.59, H 5.24, N 19.17; found: C 75.44, H 5.18, N 19.14.

5. *8,21-Bis[(6′-methyl-2,2′-bipyridin-6-yl)methyl]-8,21,27,28,29,30-hexaazapentacyclo[21.3.1.1^{2,6}.1^{10,14}.1^{15,19}]triaconta-1(27),2,4,6(30),10,12,14(29),15,17,19(28),23,25-dodecaene* (**7**) was synthesized according to the procedure used for **6** from 6-(bromomethyl)-6′-methyl-2,2′-bipyridine [10] (**10b**; 140 mg, 0.53 mmol) and **12** (100 mg, 0.25 mmol). Yield 71%. M.p. > 260°. ^{1}H-NMR (D_2O/DCl/*t*-BuOH): 8.34–7.70 (16-line *m*, 16 H); 7.28–6.88 (*m*, 8 H); 4.93–3.84 (*m*, 12 H); 2.66 (*s*, 6 H). ^{13}C-NMR (D_2O/DCl/*t*-BuOH): 158.76; 157.99; 156.00; 155.70; 154.96; 154.77; 138.71; 136.91; 136.79; 125.08; 124.37; 123.28; 120.10; 119.64; 118.19; 58.03; 55.98; 24.65. FAB-MS

(positive mode): 759.4 (15, $[M + H]^+$), 577.3 (15, $[M + H - CH_2\text{–bpy}]^+$). Anal. calc. for $C_{48}H_{42}N_{10}$: C 75.96, H 5.58, N 18.46; found: 75.79, H 5.47, N 18.38.

6. *Di(*tert*-butyl) 6-(Bromomethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxylate* (**11b**). A mixture of **11a** [64] (2.0 g, 5.2 mmol), NBS (0.93 g, 5.2 mmol), and dibenzoyl peroxide (10 mg) was heated at 80° in CCl_4 (50 ml) for 8 h under light irradiation (tungsten lamp, 100 W). The mixture was cooled to r.t., filtered over *Celite* and evaporated. The residue was chromatographed (silica gel, 1% MeOH/CH_2Cl_2): 0.62 g (26%) of **11b**. Pale-brown powder. TLC (SiO_2, 2% MeOH/CH_2Cl_2): R_f 0.71. M.p. 165°. ^{1}H-NMR ($CDCl_3$): 8.79 (*s*, 1 H); 8.68 (*s*, 1 H); 7.95 (*s*, 1 H); 7.68 (*s*, 1 H); 4.68 (*s*, 2 H); 2.70 (*s*, 3 H); 1.63 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$): 164.47; 163.89; 159.05; 157.29; 141.57; 122.89; 122.76; 119.94; 117.94; 33.52; 28.07; 24.50. Anal. calc. for $C_{22}H_{27}BrN_2O_4$: C 57.02, H 5.87, N 6.05; found: C 56.92, H 5.43, N 6.02.

7. *Di(*tert*-butyl) 6-(Azidomethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxylate* (**11c**). A mixture of **11b** (0.4 g, 0.86 mmol) and NaN_3 (0.56, 8.6 mmol) in DMSO (10 ml) was heated at 80° for 4 h. The mixture was cooled to r.t. and H_2O (50 ml) added. The white solid was filtered off and washed with H_2O (3 × 10 ml) and Et_2O (3 × 25 ml): **11c** (0.3 g, 82%) was used without further purification. TLC (Al_2O_3, 2% MeOH/CH_2Cl_2): R_f 0.83. IR (KBr): 1716 (ester), 2089 (N_3). ^{1}H-NMR (CD_2Cl_2): 8.83 (*s*, 1 H); 8.69 (*s*, 1 H); 7.80 (*s*, 1 H); 7.71 (*s*, 1 H); 4.57 (*s*, 2 H); 2.69 (*s*, 3 H); 1.63 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$): 164.50; 163.92; 159.09; 157.33; 141.60; 122.91; 122.78; 119.97; 117.98; 33.55; 28.09; 24.54.

8. *Di(*tert*-butyl) 6-(Aminomethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxylate* (**11d**). A mixture of **11c** (0.2 g, 0.47 mmol) and 5% Pd/C (10 mg) in EtOH (50 ml) was stirred under H_2 (1 atom) at r.t. for 1 night. After filtering through *Celite*, evaporation afforded **11d** (0.13 g, 70%) which was used withouth further purification. TLC (Al_2O_3, 2% MeOH/CH_2Cl_2): R_f 0.13. ^{1}H-NMR (CD_2Cl_2): 8.71 (*s*, 1 H); 8.67 (*s*, 1 H); 7.80 (*s*, 1 H); 7.68 (*s*, 1 H); 4.13 (*s*, 2 H); 2.69 (*s*, 3 H); 2.06 (*s*, 2 H); 1.63 (*s*, 9 H); 1.61 (*s*, 9 H). ^{13}C-NMR (CD_2Cl_2): 164.32; 163.90; 159.06; 157.23; 141.60; 122.73; 122.71; 119.86; 117.89; 33.47; 28.00; 24.43.

9. *Tris[(6'-methyl-4,4'-bis[*(tert*-butoxy)carbonyl]-2,2'-bipyridin-6-yl)methyl]amine* (= *Hexa(*tert*-butyl) 6',6''',6''''-Trimethyl-6,6'',6''''-[nitrilotris(methylene)]tris[2,2'-bipyridine]-4,4',4'',4''',4'''',4''''-hexacarboxylate*; **8**). To a mixture of **11d** (100 mg, 0.25 mmol) and Na_2CO_3 (530 mg, 5 mmol) in freshly distilled MeCN (100 ml) heated at reflux, a soln. of **11b** (232 mg, 0.50 mmol) in CH_2Cl_2 (15 ml) was added dropwise over 1 h. The mixture was refluxed for further 24 h. After cooling to r.t., the insoluble solid was filtered off, the filtrate evaporated, and the residue chromatographed (silica gel, 1% MeOH/CH_2Cl_2), giving **8** (glass) as main product (220 mg, 76%). ^{1}H-NMR (CD_2Cl_2): 8.73 (*s*, 3 H); 8.66 (*s*, 3 H); 8.12 (*s*, 3 H); 7.67 (*s*, 3 H); 4.28 (*s*, 6 H); 2.69 (*s*, 9 H); 1.58 (*s*, 27 H); 1.57 (*s*, 27 H). ^{13}C-NMR ($CDCl_3$): 164.41; 164.23; 160.09; 158.79; 156.06; 155.90; 141.01; 140.41; 122.42; 121.54; 118.85; 117.61; 60.31; 27.90; 24.46. FAB-MS: 1164.5 (53, $[M + H]^+$). Anal. calc. for $C_{66}H_{81}N_7O_{12}$: C 68.08, H 7.01, N 8.42; found: C 67.93, H 6.92, N 8.36.

10. *{Tris[(2,2'-bipyridin-6-yl)methyl]amine}ruthenium(II) Bis(hexafluorophosphate(V))* ([Ru(**1**)][PF_6]$_2$; **13a**). To a 'ruthenium blue solution' [42] [43] (prepared in a glass bomb with $RuCl_3 \cdot 3H_2O$ (75 mg, 0.287 mmol), platinum black (*ca.* 2 mg) in MeOH (30 ml), and H_2 (*ca.* 2 atm.)), a soln. of **1** (150 mg, 0.286 mmol) in MeOH (5 ml) was added. The mixture was heated at 100° for 15 h. After cooling to r.t., the insoluble solid was filtered over *Celite* and the complex precipitated with $NH_4[PF]_6$. The precipitate was filtered off, washed with MeOH and Et_2O, and dried. Recrystallization from acetone/Et_2O yielded **13a** (200 mg, 77%). UV/VIS (MeCN): 250 (20750), 295 (44260), 462 (9600). ^{1}H-NMR (CD_3CN): 8.43 (*d*, J = 8.0, 3 H, H–C(3')); 8.30 (*d*, J = 8.0, 3 H, H–C(3)); 7.97 (*td*, J = 7.6, 1.4, 3 H, H–C(4')); 7.89 (*t*, J = 7.8, 3 H, H–C(4)); 7.31 (*d*, J = 7.6, 3 H, H–C(5)); 7.24 (*td*, J = 5.7, 1.4, 3 H, H–C(5')); 7.06 (*d*, J = 5.7, 3 H, H–C(6')); 4.10 (*AB*, J = 17.2, 3 H); 3.86 (*AB*, J = 17.2, 3 H); proton relaxation time in s: T_1 1.26 (H–C(3')); 1.29 (H–C(3)); 2.45 (H–C(4')); 2.50 (H–C(4)); 2.25 (H–C(5)); 2.48 (H–C(5')); 3.07 (H–C(6')); 0.58 (CH_2). ^{13}C-NMR (CD_3CN): 165.98; 158.25; 157.59; 150.56; 137.68; 137.47; 126.49; 125.91; 124.76; 121.67; 54.46. Anal. calc. for [Ru(**1**)][PF_6]$\cdot$1.5 H_2O ($C_{33}H_{30}F_{12}N_7O_{1.5}P_2Ru$): C 42.17, H 3.19, N 10.44; found: C 42.27, H 3.13, N 10.34.

11. *{Tris[(2,2'-bipyridin-6-yl)methyl]amine}iron(II) Sulfate* ([Fe(**1**)]SO_4; **13b**). To a suspension of **1** (70 mg, 0.134 mmol) in EtOH (20 ml) at 60°, a soln. of $FeSO_4 \cdot 7H_2O$ (38 mg, 0.137 mmol) in H_2O (20 ml) was added. The deep-red mixture was heated at 60° for 2 h. After cooling to r.t., the soln. was filtered over *Celite* and evaporated. The residue was dissolved in EtOH (30 ml) and the complex precipitated by addition of Et_2O. Recrystallization from EtOH/Et_2O yielded **13b** (82 mg, 90%). UV/VIS (H_2O): 245 (22200), 297 (26100), 502 (1150). FAB-MS (positive mode; thio.): 674 (24, $[M + H]^+$). Anal. calc. for [Fe(**1**)$SO_4 \cdot 3H_2O$ ($C_{33}H_{33}FeN_7O_7S$): C 54.43, H 4.54, N 13.47; found: C 54.52, H 4.60, N 13.39.

12. *{Tris[(2,2'-bipyridin-6-yl)methyl]amine}chromium(II) Perchlorate* ([Cr(**1**)](ClO$_4$)$_2$; **13c**). To a suspension of **1** (70 mg, 0.134 mmol) in Ar-flushed H_2O (10 ml), solid $CrCl_2$ (25 mg, 0.163 mmol) was added. The deep-violet soln. was stirred at r.t. for 1 night and then filtered over *Celite* and the filtrate dropwise added to a $LiClO_4$ sat. H_2O soln. The black precipitate was collected by filtration, washed with cold H_2O and Et_2O and dried under high vacuum. The highly air-sensitive **13c** was used without further purification and stored under inert atmosphere in a dry-box (92 mg, 88%). UV/VIS (MeCN; under Ar): 297 (24720), 475 (1700), 551 (1750). Anal. calc. for [Cr(**1**)](ClO$_4$)$_2$ ($C_{33}H_{27}Cl_2CrN_7O_8$): C 51.31, H 3.52, N 12.69; found: C 51.17, H 3.43, N 12.78.

13. *{Tris[(2,2'-bipyridin-6-yl)methyl]amine}chromium(III) Perchlorate* ([Cr(**1**)](ClO$_4$)$_3$; **13d**). O_2 was bubbled for 1 h through a deep-violet soln. of **13c** (50 mg, 0.065 mmol) in H_2O (25 ml). The clear green soln. was concentrated to *ca.* 1 ml. The complex was precipitated by addition of 1 drop of a $LiClO_4$-sat. H_2O soln. The green precipitate was collected by filtration, washed with cold H_2O and Et_2O and dried under high vacuum: **13d** (53 mg, 93%). UV/VIS (H_2O): 280 (16340), 319.5 (18860), 640 (140). FAB-MS (positive mode, NBA): 771 (100, [Cr(**1**)](ClO$_4$)$_2$]$^+$). Anal. calc. for [Cr(**1**)](ClO$_4$)$_3$·0.5 H_2O ($C_{33}H_{28}Cl_3CrN_7O_{12.5}$): C 45.04, H 3.09, N 11.14; found: C 45.26, H 3.15, N 10.97.

14. *{μ_6-Tris[(2,2'-bipyiridin-6-yl)methyl]amine}tris[bis(2,2'-bipyridine)ruthenium(II)] Hexakis(hexafluorophosphate(V))* ([{Ru(bpy)$_2$}$_3$(**1**)][PF$_6$]$_6$; **14a**). To a soln. of *cis*-[RuCl$_2$(bpy)$_2$]·2H_2O [48] (150 mg, 0.288 mmol) in MeOH (50 ml), a suspension of **1** (50 mg, 0.096 mmol) in MeOH (20 ml) was added. The mixture was refluxed for 2 days, until [RuCl$_2$(bpy)$_2$] was no more observed by TLC (alumina, 10% MeOH/CH_2Cl_2, R_f 0.49). After cooling to r.t., the deep-orange soln. was concentrated to *ca.* 10 ml, filtered over *Celite*, and the complex precipitated by addition of a $NH_4[PF_6]$-sat. MeOH soln. The orange complex was recovered by filtration, washed with cold MeOH (*ca.* 5 ml) and Et_2O, and dried under high vacuum. Recrystallization in MeCN/Et_2O afforded a diastereoisomeric mixture **14a** (160 mg, 64%). UV/VIS (MeCN): 244 (63600), 285 (196100), 446 (33000). Anal. calc. for [{Ru(bpy)$_2$}$_3$(**1**)][PF$_6$]$_6$ ($C_{93}H_{75}F_{36}N_{19}P_6Ru_3$): C 42.44, H 2.87, N 10.11; found: C 42.65, H 2.99, N 10.02.

15. *{μ_6-Tris[(2,2'-bipyridin-6-yl)methyl]amine}tris[tricarbonylchlororhenium(I)]* ([{ReCl(CO)$_3$}(**1**)]; **14b**). To a soln. of [ReCl(CO)$_5$] [41] [49] (122 mg, 0.337 mmol) in toluene (50 ml) heated at 80°, a hot soln. of **1** (50 mg, 0.096 mmol) in toluene (5 ml) was added dropwise over 10 min. The mixture was heated at 80° for 1 further h. After cooling to 4° during 1 h, the yellow solid was filtered off, washed with toluene (2 × 5 ml) and Et_2O (3 × 20 ml), and dried under high vacuum. Recrystallization in MeCN/Et_2O afforded a diastereoisomeric mixture **14b** (130 mg, 94%). UV/VIS (MeCN): 232 (54930), 308 (42950), 360 (6490). IR (KBr): 2020, 1915, 1890 (CO). Anal. calc. for [{ReCl(CO)$_3$}$_3$(**1**)] ($C_{42}H_{27}Cl_3N_7O_{13}Re_3$): C 33.57, H 1.81, N 6.53; found: C 33.64, H 1.84, N 6.45.

16. *{1,4,7,10,13,16-Hexakis[(2,2'-bipyridin-6-yl)methyl]-1,4,7,10,13,16-hexaazacyclooctadecane}iron(II) Perchlorate* ([Fe(**4**)](ClO$_4$)$_2$; **15**). To a soln. of **4** (60 mg, 0.047 mmol) in acetone (5 ml), a soln. of $FeSO_4 \cdot 7H_2O$ (13 mg, 0.047 mmol) in H_2O (2 ml) was added dropwise. After 2 h stirring at r.t., the deep-red soln. was filtered over *Celite* and evaporated. The residue was dissolved in acetone (15 ml) and the complex precipitated by addition of few drops of a $LiClO_4$-sat. H_2O soln. Recrystallization from EtOH/Et_2O yielded **15** (68 mg, 95%). UV/VIS (MeCN): 239 (22100), 291 (45300), 368.5 (3570), 498 (sh), 524 (sh), 572.5 (4650). FAB-MS (positive mode, thio): 1422.0 (16, [[Fe(**4**)]ClO$_4$]$^+$), 1324.2 (30, [[Fe(**4**)]]$^+$). Anal. calc. for [Fe(**4**)](ClO$_4$)$_2$·3H_2O ($C_{78}H_{78}Cl_2FeN_{18}O_8$): C 59.44, H 5.33, N 16.00; found: C 59.14, H 5.20, N 16.14.

17. *{1,4,7,10,13,16-Hexakis[(2,2'-bipyridin-6-yl)methyl]-1,4,7,10,13,16-hexaazacyclooctadecane}diiron(II) Sulfate* ([Fe$_2$(**4**)](SO$_4$)$_2$·**16**). To a soln. of **4** (58 mg, 0.0458 mmol) in EtOH (20 ml) at 60°, a soln. of $FeSO_4 \cdot 7H_2O$ (26 mg, 0.0935 mmol) in H_2O (15 ml) was added dropwise. After cooling to r.t., the soln. was filtered over *Celite* and addition of pentane caused the crystallization of deep-violet **16** (71 mg, 92%). UV/VIS (H_2O): 246 (21900), 302.5 (47700), 365 (6100), 520 (sh), 559 (9500). FAB-MS (positive mode): 1572 (65, [Fe$_2$(**4**)(SO$_4$)$_2$H]$^+$, with an isotopic profile containing 2 Fe-atoms), 1510.4, 1475.4. Anal. calc. for [Fe$_2$(**4**)](SO$_4$)$_2$·4H_2O·EtOH ($C_{80}H_{92}Fe_2N_8O_{13}S_2$): C 56.87, H 5.49, N 14.92; found: C 56.91, H 6.03, N 14.76.

18. *Tris{N,N,N'N'-tetrakis[(2,2'-bipyridin-6-yl)methyl]ethylenediamine}tetrairon Sulfate* ([Fe$_4$(**2**)$_3$](SO$_4$)$_4$; **17**). To a soln. of **2** (58 mg, 0.079 mmol) in EtOH (25 ml) at 60°, a soln. of $FeSO_4 \cdot 7H_2O$ (30 mg, 0.108 mmol) in H_2O (20 ml) was added dropwise. The deep-red mixture was heated at 60° for 1 h. After cooling to r.t., the soln. was filtered over *Celite* and evaporated. The residue was dissolved in EtOH/H_2O 10:1 and the complex precipitated by pentane addition. Recrystallization from EtOH/H_2O/pentane yielded deep-violet **17** (72 mg, 93%). UV/VIS (H_2O): 237.5 (108200), 291.5 (148000), 301.5 (145600), 361.5 (15500), 520 (sh), 560 (20400). Anal. calc. for [Fe$_4$(**2**)$_3$](SO$_4$)$_4$·8H_2O ($C_{138}H_{136}Fe_4N_{30}O_{24}S_4$): C 56.13, H 4.60, N 14.24; found: C 56.30, H 5.09, N 13.76.

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