

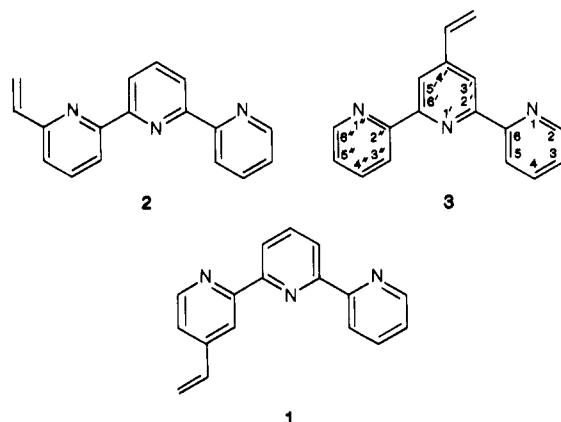
4-Vinyl-, 6-Vinyl-, and 4'-Vinyl-2,2':6',2''-terpyridinyl Ligands: Their Synthesis and the Electrochemistry of Their Transition-Metal Coordination Complexes

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Abstract: 4'-Vinyl-2,2':6',2''-terpyridinyl was conveniently prepared from 2-acetylpyridine via α -oxoketene dithioacetal methodology, the intermediate 4'-(methylthio)-2,2':6',2''-terpyridinyl being converted into the corresponding 4'-methyl derivative with methylmagnesium bromide and bis(triphenylphosphino)nickel(II) dichloride followed by generation of the methyl anion with lithium tetramethylpiperidide, reaction of the anion with chloromethyl methyl ether, and introduction of the vinyl group by treatment of the ether with potassium *tert*-butoxide/THF. Analogous reactions led to the 4-vinyl- and 6-vinyl isomers by using the appropriate methyl-substituted 2-acetylpyridine except that in these instances desulfurization of the 4'-methylthio group with nickel boride was an additional step. These vinyl-substituted ligands formed a variety of readily electropolymerizable simple and mixed-ligand complex monomers with cobalt, ruthenium, and iron with polymerization rates whose magnitude varied with position and number of vinyl substituents.

Interest in the use of 2,2'-bipyridinyl as a ligand for transition-metal ions continues unabated,¹ and, more recently, vinyl-substituted 2,2'-bipyridinyls have been utilized² in polymer formation, in chemically modified electrode studies,^{3a-d} and in solar energy conversion.^{3a,f} The results obtained in these studies strongly suggested that analogous terpyridinyl derivatives would be of special interest.⁴ However, apart from terpyridinyl itself and several aryl-substituted derivatives,⁵ very few terpyridinyls and especially vinyl-substituted terpyridinyl ligands have been described in the literature. Their coordination chemistry, electrochemistry and polymerization chemistry remain relatively unexplored areas. In this publication we describe the first syntheses of the title ligands 1-3 and related derivatives, and their application in the preparation and electropolymerization of new simple- and mixed-ligand vinyl-2,2':6',2''-terpyridinyl coordination complex monomers.

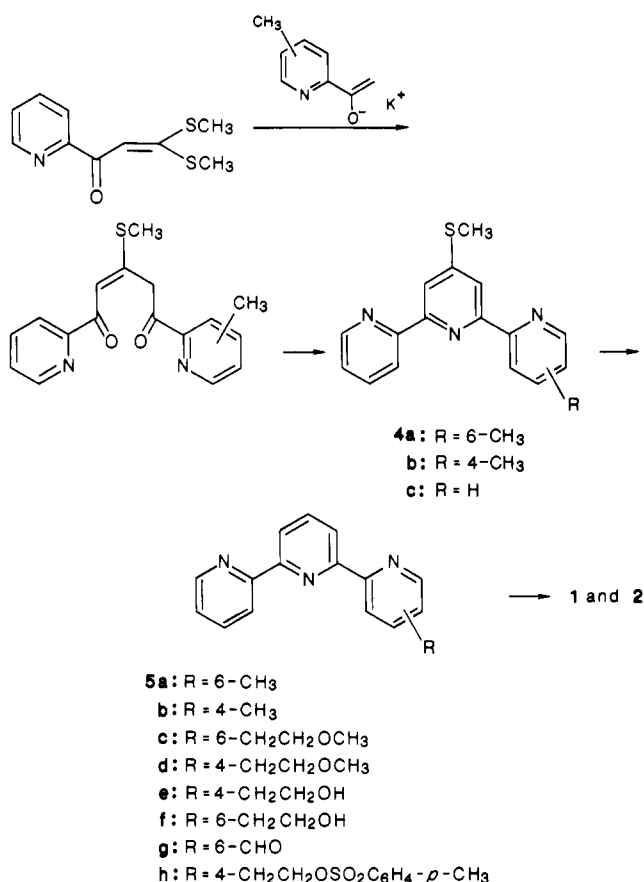


Synthesis of Ligands

The parent 2,2':2',2''-terpyridinyl ligand, although first isolated⁶ in 1932, has usually been made by coupling procedures which present obstacles when considered for the synthesis of substituted terpyridinyls. This is especially true for methyl-substituted terpyridinyls which are conceptually precursors to vinyl-substituted terpyridinyls. We have recently described⁷ the synthesis of 2,2':6',2''-terpyridinyl utilizing α -oxoketene dithioacetal methodology,⁸ and variation of this synthetic route now provides ready access to 4-, 6-, and 4'-methyl-2,2':6',2''-terpyridinyls.

4- and 6-Methyl-2,2':6',2''-terpyridinyls were prepared by reaction of 2-acetylpyridine potassium enolate with 1 equiv of carbon disulfide followed by 2 equivs of methyl iodide to give the cor-

Scheme I



responding α -oxoketene dithioacetal.⁸ Reaction of this dithioacetal with the potassium enolate of 2-acetyl-4- or 2-acetyl-6-methyl-

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Table I. Substituted 2,2':6',2''-Terpyridinyls

compd	yield, %	mp, °C	cryst habit/ recrystallization solvent ^a	mol formula ^b	<i>M</i> ⁺ (% rel int)	spectral data	
						¹ H NMR (CDCl ₃ , 200 MHz) δ	
1	78	65–66	colorless rosettes/A	C ₁₇ H ₁₃ N ₃	259 (100)	8.75–7.26 (m, 10, aromatic); 6.82 (dd, 1, H _b , <i>J</i> _{H_b-H_a} = 10.81 Hz, <i>J</i> _{H_b-H_{a'}} = 17.59 Hz); 6.07 (d, 1, H _{a'} , <i>J</i> _{H_{a'}-H_b} = 17.59 Hz); 5.54 (d, 1, H _a , <i>J</i> _{H_a-H_b} = 10.81 Hz)	
2	85	99–100	colorless needles/A	C ₁₇ H ₁₃ N ₃	259 (100)	8.79–7.28 (m, 10, aromatic); 6.88 (dd, 1, vinyl-H _b , <i>J</i> _{H_b-H_a} = 11.10 Hz, <i>J</i> _{H_b-H_{a'}} = 18.02 Hz); 6.42 (d, 1, H _{a'} , <i>J</i> _{H_{a'}-H_b} = 18.02 Hz); 5.58 (d, 1, H _a , <i>J</i> _{H_a-H_b} = 11.10 Hz)	
3	73	89–91	pale yellow rosettes/A	C ₁₇ H ₁₃ N ₃	259 (100)	8.74–7.24 (m, 10, aromatic); 6.86 (dd, 1, H _b , <i>J</i> _{H_b-H_a} = 10.89 Hz, <i>J</i> _{H_b-H_{a'}} = 17.61 Hz); 6.30 (d, 1, H _{a'} , <i>J</i> _{H_{a'}-H_b} = 17.61 Hz); 5.56 (d, 1, H _a , <i>J</i> _{H_a-H_b} = 10.89 Hz)	
4a	70	106–108	tan needles/B	C ₁₇ H ₁₅ N ₃ S	293 (100)	8.90–7.10 (m, 9, aromatic); 2.69 (s, 3, SCH ₃); 2.51 (s, 3, CH ₃)	
4b	76	97–98	gray needles/B	C ₁₇ H ₁₅ N ₃ S	293 (100)	8.70–7.10 (m, 9, aromatic); 2.65 (s, 3, SCH ₃); 1.80 (s, 3, CH ₃)	
4c	59	118–119	gray needles/A	C ₁₆ H ₁₃ N ₃ S	279 (100)	8.30–7.26 (m, 10, aromatic); 2.63 (s, 3, SCH ₃)	
5a	85	110 ^c	colorless needles/A	C ₁₆ H ₁₃ N ₃	247 (100)	8.72–6.24 (m, 10, aromatic); 2.64 (s, 3, CH ₃)	
5b	73	80	pale yellow rosettes/A	C ₁₆ H ₁₃ N ₃	247 (100)	8.90–7.04 (m, 10, aromatic); 2.51 (s, 3, CH ₃)	
5c	16 ^d	40	colorless rosettes/A	C ₁₈ H ₁₇ N ₃ O	291 (8) ^e	8.74–7.22 (m, 10, aromatic); 3.90 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.75 Hz); 3.40 (s, 3, CH ₂ CH ₂ OCH ₃); 3.16 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.75 Hz)	
5d	36 ^d	59	colorless rosettes/A	C ₁₈ H ₁₇ N ₃ O	291 (30) ^f	8.72–6.16 (m, 10, aromatic); 3.73 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.69 Hz); 3.39 (s, 3, CH ₂ CH ₂ OCH ₃); 3.02 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.69 Hz)	
5e	28	103–104	colorless rosettes/C	C ₁₇ H ₁₅ N ₃ O	277 (5) ^g	8.80–7.10 (m, 10, aromatic); 4.09 (t, 2, CH ₂ CH ₂ OH, <i>J</i> = 5.92 Hz); 3.09 (t, 2, CH ₂ CH ₂ OH, <i>J</i> = 5.92 Hz); 2.30 (s, 1, OH)	
5f	55	86–87	colorless microneedles/A	C ₁₇ H ₁₅ N ₃ O	277 (8) ^g	8.74–7.20 (m, 10, aromatic); 4.62 (s, 1, OH); 4.15 (t, 2, CH ₂ CH ₂ OH, <i>J</i> = 5.40 Hz); 3.13 (t, 2, CH ₂ CH ₂ OH, <i>J</i> = 5.40 Hz)	
5g	13	168–169	colorless needles/A	C ₁₆ H ₁₁ N ₃ O	261 (100)	10.06 (s, 1, CHO); 8.99–7.25 (m, 10, aromatic)	
5h	44	106–107	colorless needles/B	C ₂₄ H ₂₁ N ₃ O ₃ S	431 (5) ^h	8.68–7.10 (m, 14, aromatic); 4.35 (t, 2, CH ₂ CH ₂ OTs, <i>J</i> = 6.50 Hz); 3.09 (t, 2, CH ₂ CH ₂ OTs, <i>J</i> = 6.50 Hz); 2.23 (s, 3, CH ₃)	
6a	65–80	97 ⁱ	colorless needles/A	C ₁₆ H ₁₃ N ₃	247 (100)	8.66–7.24 (m, 10, aromatic); 2.45 (s, 3, CH ₃)	
6b	41 ^d	50–52	colorless needles/A	C ₁₈ H ₁₇ N ₃ O	291 (28) ^f	8.72–7.24 (m, 10, aromatic); 3.77 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.98 Hz); 3.39 (s, 3, CH ₂ CH ₂ OCH ₃); 3.09 (t, 2, CH ₂ CH ₂ OCH ₃ , <i>J</i> = 6.98 Hz)	
6c	47	166–167	colorless needles/A	C ₁₆ H ₁₁ N ₃ O	261 (100)	10.26 (s, 1, CHO), 8.92–7.37 (m, 10, aromatic)	
6d	52	50–51	colorless rosettes/C	C ₁₇ H ₁₅ N ₃ O	277 (8) ^g	8.64–7.21 (m, 10, aromatic)	

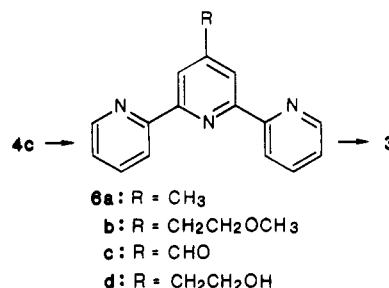
^a Abbreviations: A, *n*-hexane; B, EtOH; C, CH₃CN
^b Analytical values for C, H, and N were within ±0.17% of calculated values: ed. ^c Lit.¹⁵ mp 112–112.5 °C. ^d Purified by column chromatography [alumina/*n*-hexane:ethyl acetate (10:1)]. ^e *m/e* 276 ([*M* - CH₃], 100%). ^f *m/e* 261 ([*M* - CH₂O], 100%). ^g *m/e* 247 ([*M* - CH₂O], 100%). ^h *m/e* 172 ([*M* - OTos], 100%). ⁱ Lit.¹⁴ mp 97–100 °C.

pyridine gave the intermediate 1,5-enediones which, without attempted isolation, were subsequently converted into the terpyridinyl derivatives with hot ammonium acetate/glycolic acetic acid. Desulfurization of 4- and 6-methyl-4'-(methylthio)-2,2':6',2''-terpyridinyl (**4b** and **4a**) using nickel boride⁷ gave the desired 4- and 6-methyl-2,2':6',2''-terpyridinyl (**5b** and **5a**) in good yield (Scheme I).

In an important improvement over our published procedure, 4'-(methylthio)-2,2':6',2''-terpyridinyl (**4c**) was prepared from 2-acetylpyridine in a "one-pot" reaction in 64% overall yield (see Experimental Section). This methylthio derivative was converted into 4'-methyl-2,2':6',2''-terpyridinyl (**6a**) utilizing a recently developed⁹ nickel-catalyzed Grignard displacement reaction. Treatment of **4c** with methylmagnesium bromides in the presence of a catalytic amount of bis(triphenylphosphino)nickel(II) dichloride gave the desired 4'-methyl-2,2':6',2''-terpyridinyl (**6a**) in good yield (Scheme II).

Alkylation of the appropriate methylterpyridinyl via treatment with lithium 2,2,6,6-tetramethylpiperidide or lithium diiso-

Scheme II



propylamide in THF¹⁰ followed by the addition of chloromethyl methyl ether gave the corresponding (methoxyethyl)terpyridine derivative. Treatment of the latter with potassium *tert*-butoxide in THF produced the vinyl derivatives in good to excellent yields. These vinyl derivatives are all nicely crystalline, colorless products soluble in the majority of organic solvents and readily sublimed in vacuo (ca. 100 °C/0.01 mm). An alternative route, reaction of the anion of **5b** with formaldehyde, followed by dehydration of the alcohol **5e** or conversion of the alcohol **5e** into its tosylate **5h**, followed by elimination, resulted in **1**, but the yields were noncompetitive. Oxidation of the 4'-methyl-2,2':6',2''-terpyridinyl (**6a**) with selenium dioxide¹¹ gave the corresponding carbaldehyde **6c** which, with triphenylphosphonium methylide was converted into the 4'-vinyl derivative **3** in 15% overall yield. Difficulties in

(4) See, for example: Skorogaty, A.; Smith, T. D. *Coord. Chem. Rev.* **1984**, *53*, 55 and references therein.

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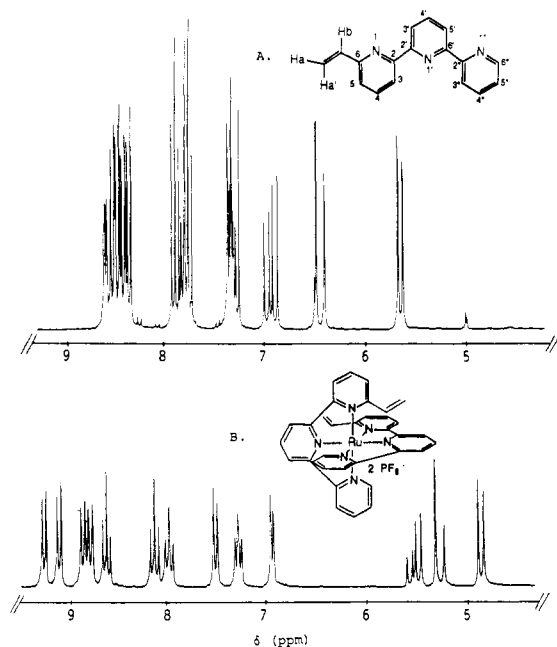


Figure 1. 200-MHz ^1H NMR spectra of (A) compound **2** and (B) $[\text{Ru}(\text{II})_2]^{2+}(\text{PF}_6^-)_2$. (Note the dramatic change in chemical shifts of the protons in **1B**.)

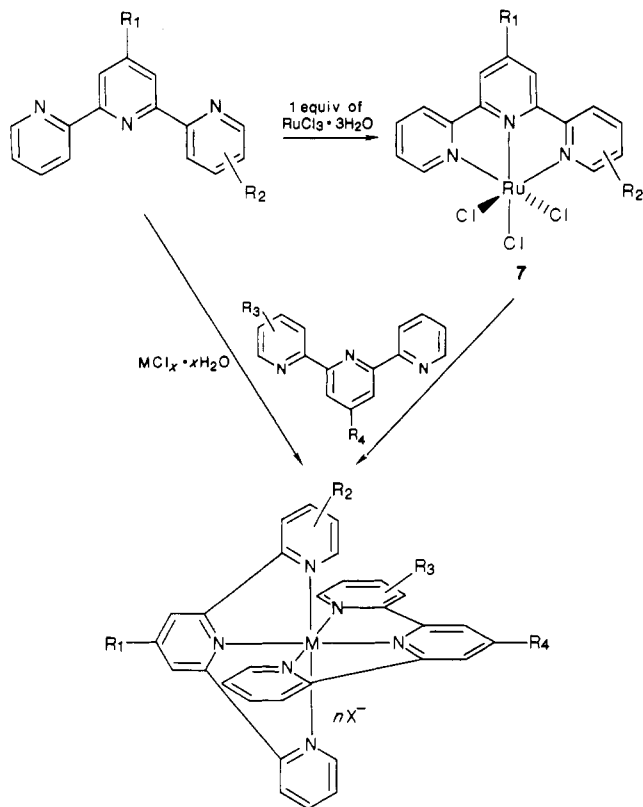
improving the yield (47%) in the SeO_2 oxidation step and the low yield (31%) obtained in the Wittig reaction make this approach unsuitable. However, the use of chloromethyl benzyl ether to form the corresponding 4'-(benzyloxy)ethyl derivative of terpyridinyl resulted in an improved yield of the 4'-vinylterpyridinyl when the reaction was carried out without isolation of the (benzyloxy)ethyl derivative. Details of these procedures are described in the Experimental Section.

Physical and analytical data for the terpyridinyls prepared are listed in Table I.

Coordination Complexes of Substituted 2,2':6',2''-Terpyridinyls

2,2':6',2''-Terpyridinyl acts as a terdentate chelation agent¹² when coordinating to transition-metal ions, producing in most cases highly stable coordination complexes.^{12c} We utilized the effective chelation ability of our vinyl-2,2':6',2''-terpyridinyl ligands to synthesize new vinyl-2,2':6',2''-terpyridinyl coordination complex monomers. Reaction of 2 equiv of ligand with 1 equiv of transition-metal cation produced a variety of simple complexes **8a-g,j,k**. Mixed-ligand ruthenium(II) complexes **8h,i** were produced via reaction of (2,6':6',2''-terpyridinyl)ruthenium(III) trichloride¹³ (**7**) with the appropriately substituted terpyridinyl ligand.

Mixed-ligand cobalt(II) complexes **10a** and **10b** were formed via reaction of (2,2':6',2''-terpyridinyl)cobalt(II) dichloride (**9**), prepared¹⁷ from the corresponding bis complex, with the appropriately substituted 2,2':6',2''-terpyridinyl ligand. Physical and analytical data for all complexes prepared are described in Table II. Complexes **8g** and **10b** were characterized as cobalt(III) salts in order to obtain ^1H NMR spectra of these systems. The marked



- 8a:** M = Ru, R₁ = R₄ = vinyl, R₂ = R₃ = H
b: M = Ru, R₂ = R₃ = 6-vinyl, R₁ = R₄ = H
c: M = Ru, R₂ = R₃ = 4-vinyl, R₁ = R₄ = H
d: M = Ru, R₁ = R₄ = S-CH₃, R₂ = R₃ = H
e: M = Ru, R₂ = R₃ = 4-CH₃, R₁ = R₄ = H
f: M = Co, R₁ = R₄ = vinyl, R₂ = R₃ = H
g: M = Co, R₂ = R₃ = 4-CH₃, R₁ = R₄ = H
h: M = Ru, R₁ = R₂ = R₃ = H, R₄ = vinyl
i: M = Ru, R₁ = R₂ = R₃ = H, R₄ = S-CH₃
j: M = Fe, R₁ = R₄ = H, R₂ = R₃ = 4-CH₃
k: M = Fe, R₁ = R₄ = vinyl, R₂ = R₃ = H

effect of coordination on the chemical shift of the protons of the ligand relative to those in the complex is of diagnostic importance, and this effect¹⁸ is dramatically illustrated in Figure 1 for the Ru(II) complex **8b**.

Electrochemical Characterization of Vinylterpyridinyl Complexes

(a) Ruthenium and Iron Complexes. Four different complex monomers (**8a-c** and **8h**) were studied, differing in the number and/or location of the vinyl groups. In general, all of the complexes exhibited well-behaved electrochemical responses. Except for complex **8b** where the vinyl substituent was in position six, i.e. α to the nitrogen atom of a pyridine ring, all of these materials exhibited similar formal potentials. Values for the metal-localized oxidation process as well as the ligand-localized reduction processes are provided in supplementary material. Complex **8b** showed some differences in its electrochemical behavior, the most notable being the shift in the formal potential for oxidation to significantly more positive values ($E = +1.34$ V). This can be attributed to the reduced stability constants of terpyridinyl-metal complexes in which the terpyridinyl ligand has α -substituents.^{5d,20} In addition, the formal potential for the electropolymerized **8b** was even more positive ($E = +1.37$ V), in contrast to the other complexes in which the formal potentials for electropolymerized films were less positive than the corresponding values for the monomer in solution e.g., for **8a**, $E_{\text{surf}} = +1.21$ and $E_{\text{soln}} = +1.24$ V. Of special significance were the very large differences in the abilities of these metal

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Table II. Transition-Metal Complexes of Terpyridinyl Ligands

compd	yield, %	cryst habit/color	mol formula ^a	spectral data	
				λ_{\max} (CH ₃ CN), nm (ϵ , m)	¹ H NMR (Me ₂ SO- <i>d</i> ₆ , 200 MHz) δ
8a	67	dark red rosettes ^b	C ₃₄ H ₂₆ N ₆ Cl ₂ O ₈ Ru·H ₂ O	241 (42 200), 274 (89 000), 313 (66 200), 489 (27 500)	9.26–7.29 (m, 22, aromatic and H _b); 6.80 (d, 2, H _a); 5.94 (d, 2, H _a)
8b	64	dark red rosettes ^b	C ₃₄ H ₂₆ H ₆ Cl ₂ O ₈ Ru	276 (27 692), 315 (42 564), 477 (10 256)	9.28–6.93 (m, 20, aromatic); 5.59 (dd, 2, H _b , J _{H_b-H_a'} = 17.49 Hz, J _{H_b-H_a} = 11.04 Hz); 5.37 (d, 2, H _a); 4.96 (d, 2, H _a , J _{H_a-H_b} = 11.04 Hz)
8c	70	dark red rosettes ^b	C ₃₄ H ₂₆ N ₆ Cl ₂ O ₈ Ru·H ₂ O	228 (62 821), 272 (41 026), 316 (66 666), 481 (15 385)	9.23–7.38 (m, 20, aromatic); 6.90 (dd, 2, H _b , J _{H_b-H_a'} = 17.56 Hz, J _{H_b-H_a} = 10.93 Hz); 6.38 (d, 2, H _a); 5.71 (d, 2, H _a , J _{H_a-H_b} = 10.93 Hz)
8d	25	dark red microneedles ^c	C ₃₂ H ₂₆ N ₆ S ₂ Cl ₂ Ru·3H ₂ O	240 (27 143), 279 (47 143), 302 (44 286), 492 (15 714)	9.10–7.30 (m, 20, aromatic); 3.00 (s, 6, SCH ₃)
8e	69	bright red rosettes ^b	C ₃₂ H ₂₆ N ₆ Cl ₂ O ₈ Ru	270 (29 452), 308 (56 164), 476 (12 329)	9.15–7.13 (m, 20, aromatic); 2.42 (s, 6, CH ₃)
8f	93	dark brown microneedles ^b	C ₃₄ H ₂₆ N ₆ P ₂ F ₁₂ Co·H ₂ O	202 (61 500), 253 (37 500), 275 (49 300), 281 (49 100), 324 (22 500), 444 (450), 520 (402)	na ^e
8g	65	gold microneedles ^b	C ₃₂ H ₂₆ N ₆ O ₁₂ Cl ₃ Co·H ₂ O	276 (39 800), 336 (17 530), 354 (10 400)	9.39–7.21 (m, 20, aromatic); 2.44 (s, 6, CH ₃)
8h	81	dark red rosettes ^b	C ₃₂ H ₂₄ N ₆ Cl ₂ O ₈ Ru	273 (58 974), 309 (66 666), 483 (20 513)	9.29–7.22 (m, 22, aromatic and H _b); 6.85 (d, 1, H _a); 5.99 (d, 1, H _a)
8i	59	dark red microneedles ^c	C ₃₁ H ₂₄ N ₆ SBr ₂ Ru·3H ₂ O	273 (60 800), 307 (74 000), 486 (22 900)	9.18–7.22 (m, 21, aromatic); 2.99 (s, 3, SCH ₃)
8j	77	dark purple rosettes ^d	C ₃₂ H ₂₆ N ₆ FeI ₂ ·H ₂ O	247 (32 500), 274 (20 000), 282 (18 300), 320 (30 800), 370 (2100), 555 (7100)	9.30–6.80 (m, 20, aromatic); 2.50 (s, 6, CH ₃)
8k	84	dark purple rosettes ^b	C ₃₄ H ₂₆ N ₆ FeP ₂ F ₁₂ ·H ₂ O	249 (16 220), 281 (32 230), 323 (19 820), 256 (9000)	9.42–7.15 (m, 22, aromatic and H _b); 6.95 (d, 2, H _a); 6.05 (d, 2, H _a)
10a	91	dark brown microneedles ^b	C ₃₂ H ₂₄ N ₆ P ₂ F ₁₂ Co	275 (49 383), 279 (50 000), 318 (35 185), 445 (1852), 510 (1605)	na ^e
10b	78	gold microneedles ^b	C ₃₁ H ₂₄ N ₆ SP ₃ F ₁₈ Co	277 (34 400), 324 (16 800), 338 (17 600), 354 (16 000)	9.42–7.43 (m, 21, aromatic); 3.05 (s, 3, SCH ₃)

^aAnalytical data for C, H, and N were $\pm 0.4\%$ of calculated values: ed. ^bRecrystallized from acetone/ether. ^cRecrystallized from H₂O. ^dRecrystallized from CH₂Cl₂/*n*-hexane. ^eCo²⁺ complexes.

complex monomers to undergo electroinitiated polymerization. Although all could be polymerized, their ability to do so varied over 2 orders of magnitude.

In order to assess the aptitude of these monomer complexes for electropolymerization, several studies were performed. Solutions of comparable concentration for the various monomers were prepared, and the potential of the electrode was scanned between 0 and -1.7 V at a rate of 200 mV/s. After a given number of scans, the electrode was removed from the solution, rinsed with acetone, and placed in a solution of acetonitrile with supporting electrolyte. The electrochemical response for the modified electrode was then obtained. Both the oxidative and reductive processes were examined. The areas under the voltammetric waves were determined to assess the coverage of polymer on the electrode surface. This polymerization ability was determined by taking the integral of the voltammetric wave (i.e. the charge) and dividing by the number of scans and the concentration used. (The electrode area was identical in all cases.)

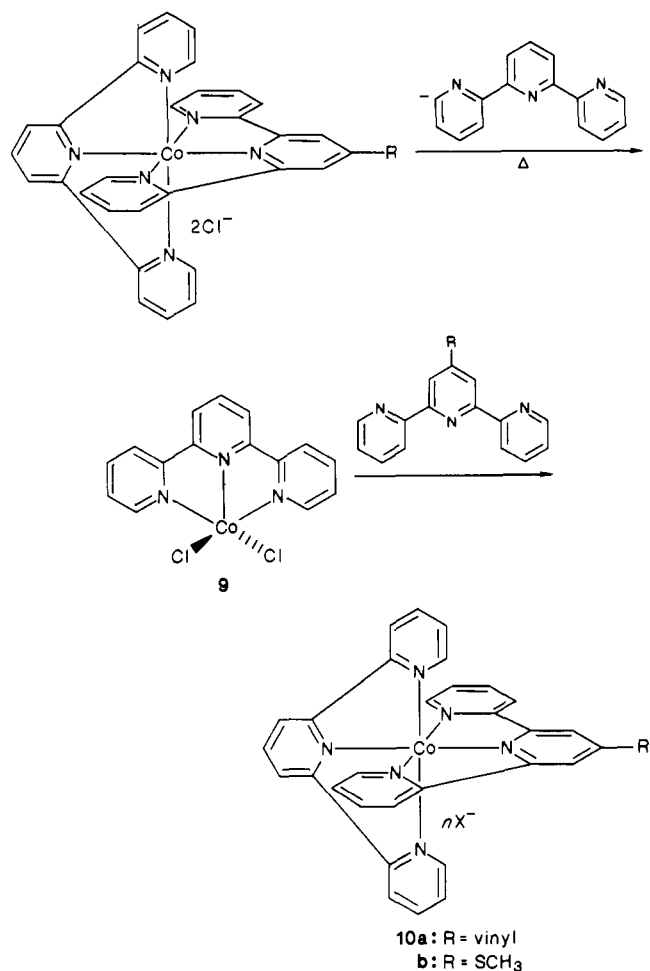
Complex **8b** with the vinyl groups α to the pyridine nitrogen had by far the slowest polymerization rate. When the values of the other complexes were normalized to that of **8b**, relative polymerization ratios were obtained. On this scale, **8b** had a relative polymerization rate of 1, **8h** had a value of 30, and both **8a** and **8c** had a relative polymerization ratio of 150. Thus, not only is the number of vinyl groups present important, but also the location of the vinyl group relative to the pyridine nitrogen plays a crucial role.

The iron complexes **8j** and **8k** exhibited well-behaved electrochemical responses, and **8k** could also be readily electropolymerized. Values for the formal potentials are in the supplementary material.

It should also be mentioned that 4'-vinyl-2,2':6',2''-terpyridinyl (**3**) itself is electroactive, but at much more negative potentials. For example, in acetonitrile/TBAP, **3** showed two reduction waves at E° values of -1.97 and -2.14 V vs. SSCE, respectively.

(b) Cobalt Complexes. Two complexes, **8f** and **10a**, were investigated, differing in that **10a** had one vinylterpyridinyl moiety whereas **8f** had two vinylterpyridinyl moieties. Both of these complexes exhibited similar responses with reversible Co(II/III) and Co(II/I) redox couples at values around $+0.26$ and -0.75 V vs. SSCE, respectively. (See supplemental material for specific values.) There was in addition a ligand-localized reduction at about -1.6 V.

In considering the electropolymerization of these monomer complexes, one needs to be aware of the nature of the redox transformations involved. The first two redox processes are metal-localized and, as a result, should not give rise to electropolymerized layers. However, due to the fact that in the Co(II)/Co(I) process the electron is localized in a metal *d* orbital that is of π -symmetry, in principle, some electron density could be delocalized over the π^* -levels of the vinyl terpyridinyl so that electropolymerization could take place. This is reinforced by the fact that terpyridinyls are moderately good π -acceptors (π -back-bonders) and so, having a metal rich center [e.g. Co(I)], could result in electron density being delocalized to the vinyl group of the terpyridinyl with subsequent electropolymerization. In fact, such an effect, although small, could be observed. When the potential of an electrode in contact with an acetonitrile solution of either of the complexes was scanned between 0 and -1.0 V, after about 15–20 min there was evidence of electropolymerization. This was shown by observing the electrochemical response in a solution containing acetonitrile with supporting electrolyte only, that is, no cobalt complex in solution. The fact that waves at potentials close to those observed for the monomer complexes were obtained implies that electropolymerization took place and that the coordination environment on the cobalt center remained essentially unaltered. Under these conditions it was much more difficult to electropolymerize complex **10a** than complex **8f** since the former had only one vinyl group. We estimate from this and other experiments that complex **8f** polymerized about five times



faster than **10a**, consistent with the results obtained with the ruthenium complexes.

As mentioned above, these complexes undergo a reduction at about -1.5 to -1.6 V that we ascribe to a ligand-localized reduction process. If during the electropolymerization the potential of the electrode was scanned past this wave, very dramatic changes were observed. First of all, the polymerization accelerated drastically for both materials, but again complex **8f** polymerized about five times as fast as **10a**. More importantly, there were some very notable changes in the voltammetric response. In the very first scan (see Figure 2A) the voltammetric responses showed a couple A/A' corresponding to the Co(II/I) redox process and B/B' corresponding to the terpyridinyl-localized reduction. C' and D' are new processes. In fact, upon continued scanning, both D and C grow and they have cathodic counterparts (see Figure 2B). However, the couple D/D' stops in its growth (or apparent growth), whereas the C/C' couple continues to grow. This process continued until large coverages of the polymer were obtained.

The cyclic voltammogram of a modified electrode in acetonitrile with supporting electrolyte (see Figure 3) showed three very well-developed waves at the potentials for the A/A', C/C', and B/B' processes with only a very small wave at D/D'. If the voltammetric scan were extended to positive potentials, a small wave with a formal potential of about $+0.2$ V associated with the Co(v-terpy)₂^{3+/2+} was observed.

Reasoning by analogy to studies performed on bipyridinyl and phenanthroline complexes of cobalt,¹⁹ we ascribe the waves at D/D' to a mixed-ligand complex of cobalt having both terpyridinyls and acetonitriles coordinated to the cobalt metal center. This behavior is in marked contrast to that observed for Co(bpy)₃ complexes in which loss of one ligand occurs. Such unusual stability in the Co(v-terpy)₂ complex may have potential electrocatalytic applications, and in fact, preliminary data indicate that this complex is effective in the electrocatalytic reduction of carbon dioxide.

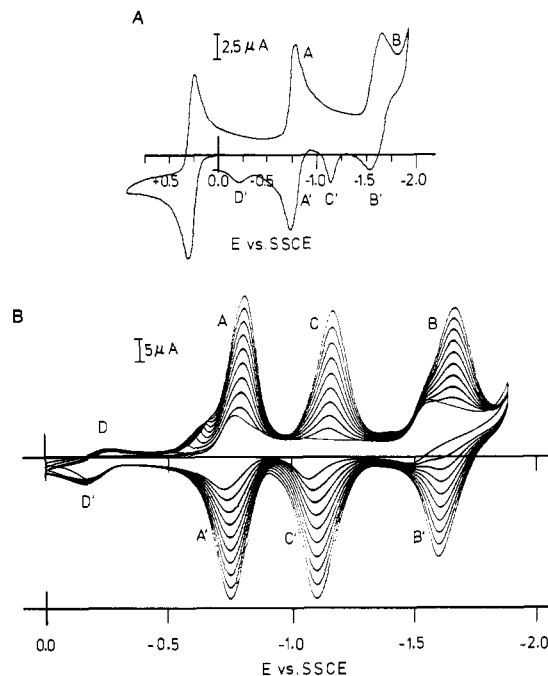


Figure 2. Cyclic voltammograms at 200 mV/s for a platinum electrode in contact with an acetonitrile/0.1 M TBAP solution containing 1 mM of complex **8f**: A, first scan; B, 10 consecutive scans.

There are in addition other effects due to differences in the electron self-exchange rate of Co(II/III) couples as opposed to Co(II/I) couples and how these affect the voltammetric response of surface immobilized redox reagents. These and other effects will be considered in a subsequent publication.

Conclusions

The availability of vinylterpyridinyl ligands via α -oxoketene dithioacetal methodology has enabled the synthesis for the first time of simple and mixed-ligand transition-metal complex monomers of Fe, Ru, and Co which all undergo electroinitiated polymerization with rates varying over 2 orders of magnitude.

The polymers derived from the Co complex monomers exhibited stability in unusual oxidation states with potential electrocatalytic applications.

Experimental Section²¹

4'-(Methylthio)-2,2':6',2''-terpyridinyl (4c). A 3-L, three-neck flask was fitted with a mechanical stirrer, an addition funnel, and a reflux condenser fitted with a nitrogen inlet. The apparatus was flame-dried and charged with potassium *tert*-butoxide (74.0 g, 0.66 mol) and anhydrous THF (500 mL). 2-Acetylpyridine (40.0 g, 0.33 mol) was next added in a dropwise fashion followed by carbon disulfide (25.1 g, 0.33 mol) and methyl iodide (93.7 g, 0.66 mol). The mixture was stirred at room temperature for 5.5 h, and additional THF (700 mL), potassium *tert*-butoxide (74.0 g, 0.66 mol), and 2-acetylpyridine (40.0 g, 0.33 mol) were then added. After the solution was stirred for 14 h at room temperature, ammonium acetate (254 g, 3.3 mol) and glacial acetic acid (400 mL) were added, and the THF was distilled off over a 4-h period. After

(21) Spectral characterizations were carried out on the following equipment: ¹H NMR, Varian XL-200; UV-vis, Cary Model 14 spectrophotometer; mass spectra, Hewlett-Packard GC-MS Model 5987A mass spectrometer. All melting points were taken in capillaries and are uncorrected. Evaporations were done under reduced pressure by using a rotatory evaporator, and microanalyses were by Atlantic Microlab Inc., Atlanta, GA. Electrochemical experiments were performed by using PAR Models 173 potentiostat, 179 digital coulometer, and 179 universal programmer or with a locally built potentiostat and signal generator combination. Data were recorded on either Soltec or Hewlett-Packard X-Y recorders. Three compartment electrochemical cells of conventional design were used throughout. All experiments were performed on platinum disk electrodes sealed in glass. Prior to use, the electrodes were polished with 1- μ m diamond paste and rinsed thoroughly with water, acetone, and methanol. Acetonitrile (Burdick and Jackson, distilled in glass) was dried over 4- \AA molecular sieves. Tetra-*n*-butylammonium perchlorate (G. F. Smith Co.) was recrystallized three times from ethyl acetate and dried in vacuo for 72 h at 75 $^{\circ}$ C before use.

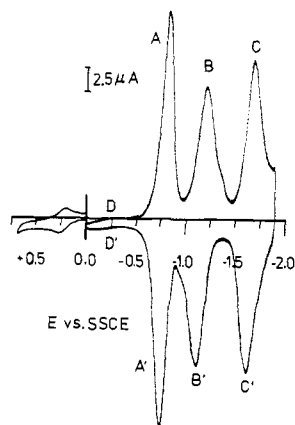


Figure 3. Cyclic voltammograms at 200 mV/s in acetonitrile/0.1 M TBAP for a platinum electrode modified with a polymeric film of complex **8f**.

being cooled to room temperature, the mixture was poured over ice (1 L), diluted with distilled water (1 L), and allowed to stand for 3 h. The gray solid was collected by suction filtration and, after drying in the funnel, was placed in a thimble and extracted into hot hexane (2 days). Upon cooling, off-white needles separated: 54.6 g (59%); mp 119 °C. The above aqueous filtrate was extracted with CHCl_3 (1 L), and the CHCl_3 extract was dried (anhydrous Na_2SO_4); removal of the CHCl_3 left a dark oil which crystallized from *n*-hexane: 4.6 g (5%); mp 118 °C. The total yield was 59.2 g (64%); mp 118–119 °C (lit.⁸ mp 118–119 °C).

General Procedure for Desulfurizations. Preparation of 6-Methyl-2,2':6',2''-terpyridinyl (5a). A 1-L three-neck flask was fitted with a mechanical stirrer, a pressure-equalizing addition funnel, and a reflux condenser. The flask was purged with nitrogen and charged with absolute ethanol (300 mL), nickel(II) dichloride hexahydrate (56.8 g, 239 mmol) and 4'-(methylthio)-6-methyl-2,2':6',2''-terpyridinyl (**4a**) (7.0 g, 23.9 mmol). The reaction was stirred at room temperature for 10 min after which sodium borohydride (168 mL of a 4.4 M solution in NaOH, 0.74 mol) was added slowly, keeping heating and frothing to a minimum. The deep blue solution was allowed to de-gas and was then heated under reflux for 12 h. The reaction was poured while boiling through a 2-in. Celite pad, and the collected black nickel salts were washed with copious quantities of hot ethanol. The filtrate was concentrated to a viscous mull which was poured into ice water (1 L) and left to stand for 3 h. The resultant mixture was extracted with CHCl_3 (700 mL) and the CHCl_3 extract dried (Na_2SO_4). Removal of the CHCl_3 afforded a pale yellow solid which was subsequently dissolved in chloroform and passed through a short alumina column using hexane/ether (20:1) as eluent. Removal of the solvent left a colorless solid which crystallized from *n*-hexane as colorless needles: 5.0 g (85%); mp 110 °C (lit.¹⁵ mp 112.5 °C); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1560 and 1580 cm^{-1} .

Preparation of 4'-Methyl-2,2':6',2''-terpyridinyl (6a). A 1-L three-neck flask was fitted with a nitrogen inlet and a septum. The flask was flame-dried and charged with anhydrous ether (40 mL) and bis(triphenylphosphino)nickel(II) dichloride (1.47 g, 2.25 mmol). Methylmagnesium bromide (13.5 mL of a 2.57 M solution in ether, 34.6 mmol) was next injected into the solution whose color became deep purple-brown. The reaction mixture was stirred at room temperature for 15 min after which **4c** (4.0 g, 14.3 mmol) in ether (400 mL) was injected into the reaction mixture whose color immediately changed to pale green. After being heated under reflux with stirring for 48 h, the cooled reaction mixture was poured over saturated aqueous NH_4Cl solution (200 mL). The black precipitate was filtered off and washed with CHCl_3 . The aqueous phase was extracted with CHCl_3 , and the organic phases were combined and dried (Na_2SO_4). Removal of solvent produced a dark green, oily solid which was boiled in *n*-hexane and filtered. Concentration of the filtrate afforded a pale green solid which was dissolved in CHCl_3 and passed through a short alumina flash column and eluted with *n*-hexane/ether (10:1). Removal of the solvent gave a pale yellow solid which, after recrystallization from *n*-hexane, afforded cream rosettes: 2.60 g (80%); mp 89 °C¹⁶ (lit.¹⁴ mp 97–100 °C); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1560, 1580 cm^{-1} .

General Procedure for the Synthesis of Terpyridinyl Aldehydes. Preparation of 2,2':6',2''-Terpyridinyl-4'-carboxaldehyde (6c). A 250-mL round-bottom flask was fitted with a reflux condenser and charged with glacial acetic acid (100 mL), selenium dioxide (900 mg, 8.10 mmol), and **6a** (1.0 g, 4.0 mmol). The mixture was heated under reflux for 48 h, the gray selenium metal was removed by filtration, and the filtrate was neutralized with 10% aqueous sodium hydroxide. The aqueous layer was

extracted with CHCl_3 (300 mL), and, after the solution was dried (Na_2SO_4), the CHCl_3 was removed by evaporation leaving a dark green residue. Recrystallization from *n*-hexane afforded colorless needles: 470 mg (47%); IR (KBr) ν_{CHO} 1700 cm^{-1} , $\nu_{\text{C}=\text{N}}$ 1550, 1580 cm^{-1} .

General Procedure for the Preparation of (2-Hydroxyethyl)-2,2':6',2''-terpyridinyls. Synthesis of 4-(2-Hydroxyethyl)-2,2':6',2''-terpyridinyl (5e). A 500-mL three-neck flask was fitted with a septum, a nitrogen inlet, and a mechanical stirrer. The apparatus was flame-dried and charged with 60 mL of dry THF. Diisopropylamine (1.3 mL, 9.0 mmol) was injected into the reaction mixture followed by *n*-butyllithium (4.50 mL of a 2.00 M solution in hexane, 9.0 mmol), and the mixture was stirred for 15 min at room temperature. 4-Methyl-2,2':6',2''-terpyridinyl (**5b**) (2.0 g, 8.1 mmol) in dry THF (80 mL) was added dropwise to the solution whose color immediately changed to deep purple, and the mixture was stirred at room temperature for an additional hour. Formaldehyde (gas) was next bubbled into the reaction mixture, whose color gradually changed to pale green. The solution was stirred for 7 h, and then the excess LDA was decomposed with some 90% ethanol. The mixture was poured onto ice (500 mL) and allowed to stand for 2 h. All THF was removed, and the remaining aqueous mixture was extracted with CHCl_3 (400 mL) and the CHCl_3 extract dried (Na_2SO_4). Removal of the solvent left a dark oil which was taken up in boiling acetonitrile and filtered. After in vacuo removal of the CH_3CN , the remaining oil was passed through a short alumina column and eluted with CHCl_3 . Removal of solvent afforded a light orange oil which crystallized from acetonitrile as colorless rosettes: 630 mg (28%); mp 103–104 °C; IR (KBr) ν_{OH} 3499–3095 cm^{-1} .

4-(2-(*p*-Tolylsulfonyl)oxy)ethyl)-2,2':6',2''-terpyridinyl (5h). A 250-mL three-neck flask was fitted with a reflux condenser and a nitrogen inlet. The apparatus was flame dried and charged with dry benzene (75 mL), **5e** (590 mg, 2.1 mmol), and excess triethylamine. After this mixture was stirred at room temperature for 30 min, *p*-toluenesulfonyl chloride (650 mg, 3.4 mmol) was added, and the reaction mixture was heated under reflux for 4 h, then cooled to room temperature, and poured over ice (300 mL). Extraction with CHCl_3 (300 mL), drying (Na_2SO_4), and evaporation of the CHCl_3 left an orange oil. The oil was passed through a short alumina flash column and eluted with CHCl_3 . Removal of the solvent afforded a tan oil which crystallized on trituration with ethanol/water. Recrystallization from ethanol gave colorless needles: 400 mg (44%); mp 106–107 °C.

General Procedure for the Alkylation of Methyl Terpyridinyls. Preparation of 4'-(2-Methoxyethyl)-2,2':6',2''-terpyridinyl (6b). A 500-mL, three-neck flask was fitted with a septum, a pressure-equalizing addition funnel, and a nitrogen inlet. The apparatus was flame-dried and charged with **6a** (5.0 g, 20.2 mmol) and THF (100 mL). The mixture was cooled to –10 °C, and lithium 2,2,6,6-tetramethylpiperidide [prepared by injection of 2,2,6,6-tetramethylpiperidine (5.22 mL, 30.3 mmol) and methylolithium (27.5 mL of 1.1 M solution in ether, 30.3 mmol) into the addition funnel] was added dropwise to the reaction mixture whose color changed to deep red-brown. After the solution was stirred at –10 °C for 1/2 h, chloromethyl methyl ether (3.5 mL, 45.5 mmol) was injected into the reaction mixture which was stirred at –10 °C for an additional 10 h, then distilled water (100 mL) was added, and the THF was removed by evaporation. The aqueous layer was extracted with CHCl_3 (300 mL) and the extract dried (Na_2SO_4). Removal of solvent produced a dark oil which was passed through a narrow alumina column and eluted with hexane/ethyl acetate (10:1). The second fraction produced a light yellow oil which solidified and recrystallized from *n*-hexane as colorless needles: 2.40 g (41%); mp 50–52 °C.

General Procedure for the Formation of Vinylterpyridinyls. Preparation of 4'-Vinyl-2,2':6',2''-terpyridinyl (3). Method A. A 250-mL, three-neck flask was fitted with an addition funnel and a nitrogen inlet and charged with THF (50 mL) and potassium *tert*-butoxide (500 mg, 4.46 mmol). Compound **6b** (490 mg, 1.68 mmol) in THF (50 mL) was added in a dropwise fashion, and the mixture was stirred for 2 h at room temperature. Distilled water (200 mL) was then added, and all THF was removed under reduced pressure. The aqueous phase was extracted with CHCl_3 (200 mL) and the CHCl_3 extract dried (Na_2SO_4). Removal of solvent left a pale yellow solid which crystallized from *n*-hexane as cream rosettes: 320 mg (73%); mp 89–91 °C.

4-Vinyl-2,2':6',2''-terpyridinyl (1). Method B. A 250-mL, three-neck flask was fitted with a pressure-equalizing addition funnel and a nitrogen inlet. The apparatus was flame-dried and charged with dry THF (100 mL) and 4-(2-(*p*-tolylsulfonyl)oxy)ethyl)-2,2':6',2''-terpyridinyl (**5h**) (200 mg, 0.46 mmol). The reaction was cooled to 0 °C, and potassium *tert*-butoxide (56 mg, 0.50 mmol) in dry THF (50 mL) was added slowly to the reaction mixture which slowly assumed a pale green color. The mixture was stirred at 0 °C for 30 min, then water (200 mL) was added, and all the THF was removed under reduced pressure. The aqueous layer was extracted with CHCl_3 (200 mL) and the CHCl_3 layer dried (Na_2SO_4).

SO₄). Removal of the CHCl₃ under reduced pressure left a dark brown residue which crystallized from *n*-hexane affording cream rosettes: 95 mg (80%); mp 65–66 °C.

4'-Vinyl-2,2':6',2''-terpyridinyl (3). Method C. A 100-mL, three-neck flask was fitted with a pressure-equalizing addition funnel with septum, a reflux condenser, and a nitrogen inlet. The apparatus was charged with dry benzene (50 mL) followed by *n*-butyllithium (0.95 mL of 2.5 M solution in hexane, 2.2 mmol) and methyltriphenylphosphonium bromide (790 mg, 2.2 mmol). The reaction mixture gradually became homogeneous, turning a pale yellow color. After 4 h at room temperature, **6c** (520 mg, 2.0 mmol) in dry benzene (25 mL) was added to this solution in a dropwise fashion over a period of 10 min. The mixture was heated under reflux for 12 h and allowed to cool, and the phosphorus oxide salts were filtered off. The benzene was removed under reduced pressure, and the remaining oil was passed through a short alumina flash column and eluted with hexane/EtOAc (10:1). Removal of solvent left a light colored solid which recrystallized from *n*-hexane as cream rosettes: 160 mg (31%); mp 89–91 °C.

4'-Vinyl-2,2':6',2''-terpyridinyl (3). Method D. A 500-mL three-neck flask was fitted with a pressure-equalizing addition funnel, a nitrogen inlet, and a septum. The apparatus was flame-dried under nitrogen and charged with **6a** (4.40 g, 17.8 mmol) and THF (150 mL). After the mixture was cooled to –10 °C, lithium-2,2,6,6-tetramethylpiperidide [prepared from 2,2,6,6-tetramethylpiperidine (3.5 mL, 20.5 mmol) and methylolithium (18.6 mL of a 1.1 M solution in ether) (20.5 mmol)] was next added dropwise to the reaction mixture whose color changed to deep purple-brown. The reaction mixture was stirred for 3/4 h at –10 °C, and chloromethyl benzyl ether (2.90 mL, 20.5 mmol) was injected into the solution. After being stirred at –10 °C for 14 h, the reaction mixture was warmed to room temperature and stirred an additional 10 h. Dilution with water (150 mL) and removal of THF gave an aqueous solution which was extracted with CHCl₃ (250 mL), and the CHCl₃ extract was dried (Na₂SO₄). Evaporation of solvent gave a dark oil. ¹H NMR (CDCl₃, 200 MHz) showed 4'-(2-(benzyloxy)ethyl)-2,2':6',2''-terpyridinyl in high purity. This crude oil was transferred to a 500-mL, three-neck flask fitted with a pressure-equalizing addition funnel and a nitrogen inlet. THF (150 mL) was added, and the mixture was cooled to –10 °C. Potassium *tert*-butoxide (2.10 g, 18.8 mmol) in THF (200 mL) was added dropwise, and, after 2 h all THF was removed by evaporation. The aqueous solution was extracted with CHCl₃ (500 mL), and the CHCl₃ extract was dried (Na₂SO₄). Removal of the CHCl₃ produced a dark brown oil which was boiled in *n*-hexane and filtered. Reduction of the hexane volume to 50 mL and cooling produced pale yellow rosettes: mp 89–90 °C; 1.7 g (36% based on starting **6a**).

General Procedure for the Synthesis of Simple Ruthenium–Terpyridinyl Complexes. Preparation of Bis(4'-vinyl-2,2':6',2''-terpyridinyl)ruthenium(II) Perchlorate Monohydrate (8a). Compound **3** (150 mg, 0.58 mmol) and ruthenium(III) trichloride trihydrate (75 mg, 0.29 mmol) were heated in refluxing ethanol–water (4:1, 50 mL) for 5 h, producing a deep red solution. After filtering, the solution volume was reduced to ~5 mL, and saturated, aqueous sodium perchlorate solution (2 mL) was added. The dark red precipitate was collected on a frit and washed with cold ethanol. Recrystallization from acetone/ether produced dark red rosettes: IR (KBr) $\nu_{\text{C}=\text{N}}$ 1610 cm⁻¹ (m), ν_{ClO_4} 1090 cm⁻¹ (s).

Bis(4'-vinyl-2,2':6',2''-terpyridinyl)cobalt(II) Hexafluorophosphate Monohydrate (8f). Compound **3** (300 mg, 1.2 mmol) was added to

cobaltous chloride hexahydrate (140 mg, 0.59 mmol) in distilled water (30 mL) and the dark brown solution stirred for 4 h at room temperature. After the solution was filtered, ammonium hexafluorophosphate (200 mg, 1.25 mmol) in distilled water (2 mL) was added, and the light brown precipitate was collected on a frit and washed with cold ethanol. Recrystallization from acetone/ether afforded dark brown microneedles: 420 mg (93%); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1610 cm⁻¹ (m), ν_{PF_6} 850 cm⁻¹ (s).

(2,2':6',2''-Terpyridinyl)ruthenium(III) trichloride (7a) was prepared according to literature procedure¹³ in 86% yield. Similarly, (2,2':6',2''-terpyridinyl)cobalt(II) dichloride (**9**) was prepared¹⁷ in 98% yield.

General Procedure for the Synthesis of Mixed-Ligand Terpyridinyl–Ruthenium Complexes. Preparation of (2,2':6',2''-Terpyridinyl)(4'-vinyl-2,2':6',2''-terpyridinyl)ruthenium(II) Perchlorate (8h). Compound **3** (182 mg, 0.70 mmol) was added to a solution of (2,2':6',2''-terpyridinyl)ruthenium(III) trichloride (**7a**) (310 mg, 0.70 mmol) in ethanol/water (3:1, 50 mL). The mixture was heated under reflux for 4.5 h, and the deep red reaction mixture was filtered hot, allowed to cool, and diluted with ether (40 mL). Addition of saturated, aqueous sodium perchlorate solution (2 mL) resulted in a dark red precipitate which was collected on a frit. Recrystallization from acetone/ether produced dark red rosettes: 450 mg (81%); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1610 cm⁻¹ (m), ν_{ClO_4} 1090 cm⁻¹ (s).

General Procedure for the Preparation of Mixed-Ligand Terpyridinyl–Cobalt Complexes. Synthesis of (2,2':6',2''-Terpyridinyl)(4'-vinyl-2,2':6',2''-terpyridinyl)cobalt(II) Hexafluorophosphate (10a). (2,2':6',2''-Terpyridinyl)cobalt(II) dichloride (**9**) (280 mg, 0.77 mmol) was added in bulk to a solution of previously dissolved **3** (200 mg, 0.77 mmol) in ethanol/water (1:1, 40 mL). The dark brown solution was stirred for 24 h, then filtered, and treated with saturated, aqueous ammonium hexafluorophosphate (3 mL). The resultant dark brown salt was collected on a frit and washed with ether (10 mL). Recrystallization from acetone/ether produced dark brown microneedles: 590 mg (91%); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1600 cm⁻¹ (m), ν_{PF_6} 850 cm⁻¹ (s).

General Procedure for the Preparation of Cobalt(III) Complexes. Synthesis of Bis(4-methyl-2,2':6',2''-terpyridinyl)cobalt(III) Perchlorate Monohydrate (8g). Bis(4-methyl-2,2':6',2''-terpyridinyl)cobalt(II) perchlorate (1.50 g, 2.0 mmol) was added to a 0.1 M HCl solution (50 mL) which was then treated with lead dioxide (470 mg, 2.0 mmol). The mixture was heated at 50 °C for 1 h during which time the red solution assumed a gold color. After filtering, the solution was treated with aqueous sodium perchlorate (1 mL of saturated solution), and the resultant gold precipitate was collected on a frit and washed with cold water. Recrystallization from acetone/ether produced gold microneedles: 1.10 g (65%); IR (KBr) $\nu_{\text{C}=\text{N}}$ 1610 cm⁻¹ (m), ν_{ClO_4} 1090 cm⁻¹ (s).

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Supplementary Material Available: A table listing electrochemical data for metal complexes **8a–c**, **8f**, **8j–k**, and **10a** and for the free ligand **3** (1 page). Ordering information is given on any current masthead page.