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RUTHENIUM PORPHYRIN COMPLEXES CONTAINING THIOCARBONYL OR CYANIDE LIGAND

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Summary

Treatment of $Ru^{II}(OEP)CO(Py)$ with Br_2 in the presence of excess cyanide leads to oxidative decarbonylation and the formation of the isolable anion $[Ru^{III}(OEP)(CN)_2]^-$, from which the neutral complex $Ru^{III}(OEP)CN(Py)$ is readily obtained. [OEP is the dianion of octaethylporphyrin, Py = pyridine.] Reduction of the neutral (cyano)pyridine species in the presence of thiophosgene leads to the formation of $Ru^{II}(OEP)CS(Py)$. The spectroscopic and electrochemical properties of the carbonyl and thiocarbonyl compounds within the series M(OEP)CX(Py) (M = Fe, Ru, Os; X = O, S) are examined and compared. The anionic species $[Ru(OEP)CN(L)]^-$ (L = CO, Py) are also identified in solution.

Introduction

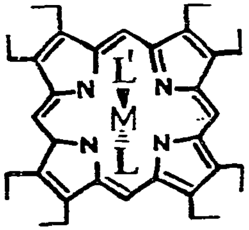
The synthesis and characterization of transition metal complexes containing the thiocarbonyl ligand, CS, continue to be of considerable interest [1—4]. Until now, however, the only examples of this ligand in porphyrin chemistry have been in the $iron^{II}$ and $osmium^{II}$ complexes, Fe(TPP)CS(L) [5] and M(OEP)-CS(L) [6] (where M = Fe and Os, TPP and OEP are the dianions of octaethylporphyrin and *meso*-tetraphenylporphyrin, respectively, and L is an amine). We report here the synthesis of a corresponding ruthenium derivative, Ru(OEP)-CS(Py) (I) and compare it to the iron and osmium derivatives listed in Table 1.

Unlike CO, carbon monosulfide (CS) is unstable and dimerizes at elevated temperature and pressure [7]. Therefore, to be of use as a ligand in the monomeric state, CS must be generated in situ. Two major synthetic methods have been developed for the incorporation of the thiocarbonyl ligand into transition metal complexes:

1) sulfur abstraction from coordinated carbon disulfide, CS_2, and
2) reduction of thiophosgene, $CSCl_2$.

TABLE 1

SOME CARBONYL, THIOCARBONYL, AND CYANO COMPLEXES OF THE IRON TRIAD



Complex	M	L′	L	Ref.
I	Ru	CS	Py	This work
II	Fe	CS	—	6
III	Os	CS	Py	6
IV	Ru	CO	Py	18,21,22,27
V	Ru	CN^-	CN^-	This work
VI	Ru	CN^-	Py	This work
VII	Ru	Py	Py	18,22,27
VIII	Fe	CS	Py	5,6
IX	Os	CO	Py	6,21,22
X	Fe	CO	Py	19,23

The first method has been used successfully [8—13] in systems where a labile ligand is displaced from the coordination sphere of the metal by CS_2. The coordinated carbon disulfide can then be converted into the thiocarbonyl ligand by the abstraction of sulfur with a thiophile such as triphenylphosphine. The second method involves the reaction of $CSCl_2$ with a reduced transition metal complex [14], or the "three fragment" oxidative addition of $CSCl_2$ to a coordinatively unsaturated compound [15].

The second method has shown the greater versatility in porphyrin chemistry and has been used to synthesize both the iron [5,6] and osmium [6] thiocarbonyl complexes according to the reactions [1—3].

$$\mathrm{Fe(TPP)Cl + CSCl_2 \xrightarrow{Na/Hg} Fe(TPP)CS + 3\ NaCl} \tag{1}$$

$$\mathrm{Fe(OEP)Cl + CSCl_2 \xrightarrow{Na/Hg} \underset{(II)}{Fe(OEP)CS} + 3\ NaCl} \tag{2}$$

$$\mathrm{Os(OEP)Br_2 + CSCl_2 \xrightarrow[THF/Py]{Na/Hg} \underset{(III)}{Os(OEP)CS(Py)} + 2\ NaBr + 2\ NaCl} \tag{3}$$

The osmium complex (III) was also prepared [6] in low yields by method 1 according to reaction 4, although the nature of the sulfur extraction in this reaction was not determined.

$$\mathrm{Os(OEP)N_2(THF) + CS_2 \xrightarrow[Pyridine]{THF} Os(OEP)CS(Py) + S} \tag{4}$$

Method 2 again proved to be the more versatile in the synthesis of Ru(OEP)CS(Py) (I).

Despite attempts at metallating porphyrins and phthalocyanines using various ruthenium complexes, we have found that $Ru_3(CO)_{12}$ is still the reagent of choice for synthesizing the porphyrins [16,17] (Scheme 1). However, although essentially quantitative metallation is observed, the resultant products are always carbonyl complexes. The high affinity of ruthenium(II) macrocycles for carbon monoxide has, in the past, required a photochemical decarbonylation [18] for the preparation of complexes axially coordinated by ligands other than CO (Scheme 1). The low quantum yields for these photochemical decarbonylations preclude facile reactions on a preparative scale. Unlike the Ru^{II} complexes, the corresponding Ru^{III} systems have a low affinity for CO and this provides for a convenient oxidative decarbonylation.

Results and discussion

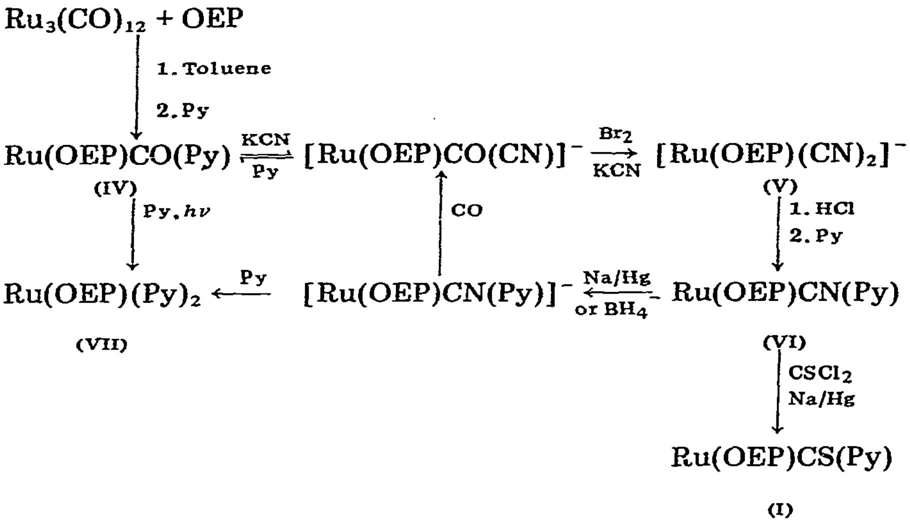
Treatment of Ru(OEP)CO(Py) (IV) with cyanide yields the anionic species $[Ru(OEP)CO(CN)]^-$. Unlike the osmium analogue [19], the ruthenium complex could not be isolated as a solid, but was identified by a very characteristic electronic absorption spectrum, particularly a red-shifted Soret band at 402 nm (cf. Table 3 below). The $[Ru(OEP)CO(CN)]^-$ anion is readily oxidized by bromine in the presence of excess cyanide to give the dicyano complex $[Ru(OEP)(CN)_2]^-$ isolated as the tetra-n-butyl ammonium salt (V). The corresponding TPP anion has been isolated previously [20]. Acidification of a methanolic solution of V, followed by evaporation and treatment of the residue with pyridine gives the preparatively useful neutral (cyano)pyridine complex Ru(OEP)CN(Py) (VI).

Reduction of VI by sodium amalgam or sodium borohydride yields solutions containing $[Ru(OEP)CN(Py)]^-$, which appears to be kinetically stable as suggested by the reversible nature of the first reduction potential observed in the cyclic voltammogram of VI (see below). The $[Ru(OEP)CN(Py)]^-$ anion reacts rapidly with CO to form the carbonylcyano species $[Ru(OEP)CO(CN)]^-$ mentioned above, and on refluxing in neat pyridine yields the bis(pyridine) adduct $Ru(OEP)(Py)_2$ (VII), previously prepared by a photodecarbonylation procedure from IV [18]. Reduction of VI with sodium amalgam in the presence of $CSCl_2$ yields the thiocarbonyl complex Ru(OEP)CS(Py) (I). The coordination chemistry described above is outlined in Scheme 1.

Like the corresponding osmium derivative (III), the ligand affinity of the Ru(OEP)CS moiety is large and a pentacoordinate species analogous to the iron complex (II) [5,6] is not observed. The mass spectra of the ruthenium and osmium thiocarbonyl complexes, I and III, show a further similarity in that the base peak is $M(OEP)CS^+$, indicating unusual strength of the metal—carbon bond. Table 2 lists the major peaks in the mass spectra of a number of the carbonyl, thiocarbonyl, and cyano complexes.

With the exception of Os(OEP)CO(Py) (IX), which shows a small peak at 831 (1% intensity) [21], none of the other compounds listed show parent peaks. The ruthenium and osmium thiocarbonyls I and III show the following

SCHEME 1



fragmentation pattern:

$$\text{M(OEP)CS(Py)}^{+\cdot} \rightarrow \text{M(OEP)CS}^{+\cdot} \rightarrow \text{porphyrin fragmentation}$$

The base peak is M(OEP)CS$^{+\cdot}$ and the metal—CS bond remains intact throughout the porphyrin fragmentation. The other complexes listed show the very different fragmentation pattern:

$$\text{M(OEP)CX(Py)}^{+\cdot} \rightarrow \text{M(OEP)CX}^{+\cdot} \rightarrow \text{M(OEP)}^{+\cdot} \rightarrow \text{porphyrin fragmentation}$$

The electronic absorption spectra of the ruthenium complexes I, IV, V and VI, are shown in Figs. 1 and 2, and the maxima are listed in Table 3. Following the trend formulated as the "Bathochromic Rule" in earlier publications on a variety of Ru and Os porphyrins [6,22—24], the thiocarbonyl complex I shows a definite red shift of the absorption maxima relative to the carbonyl complex IV. This "bathochromic shift" is also seen in the spectra of the corresponding iron and osmium complexes [6].

TABLE 2

MASS SPECTRAL DATA FOR SOME CARBONYL, THIOCARBONYL, AND CYANO COMPLEXES, M(OEP)CS(Py) [a]

Complex	M(OEP)CX$^+$	M(OEP)$^+$	M(OEP)CX^{2+}	M(OEP)$^{2+}$	Ref.
Fe(OEP)CS(Py), VIII	632(4)	588(100)	316(1)	294(17)	6
Ru(OEP)CS(Py), I	678(100)	634(7)	339(21)	317(6)	This work
Ru(OEP)CN(Py), VI	660(22)	634(100)	330(6)	317(18)	This work
Ru(OEP)(CO)(Py), IV	662(29)	634(100)	331(11)	317(42)	19
Os(OEP)CS(Py), III	768(100)	724(20)	384(17)	361(4)	6
Os(OEP)CO(Py), IX	752(20)	724(100)	375(4)	362(28)	21

[a] Mass numbers based on ^{56}Fe, ^{102}Ru, ^{192}Os; relative intensity in parentheses.

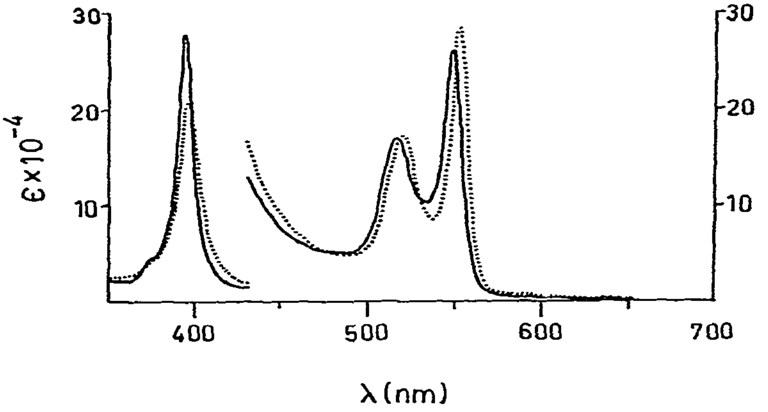


Fig. 1. Absorption spectra of Ru(OEP)CO(Py) (IV, ———), and Ru(OEP)CS(Py) (I, · · · · · ·) in CH_2Cl_2.

The bathochromic shift has been attributed to the greater π-acceptor capacity of the thiocarbonyl ligand [6,24]. The porphyrin $\pi \rightarrow \pi^*$ transitions are affected by the magnitude of metal ($d\pi$) to porphyrin (π^*) backbonding. Increasing π-acidity of the axial ligand reduces the electron density in the metal $d\pi$ orbitals and consequently reduces the extent of metal to porphyrin backbonding. This in turn lowers the energy of the porphyrin π^* orbitals and shifts the $\pi \rightarrow \pi^*$ transtiion to lower energy, which results in the observed bathochromic shifts.

The frequency difference $\Delta\nu_\alpha$ (cm^{-1}) for the α-bands of each of the carbonyl-thiocarbonyl pairs in the M(OEP)CX(Py) complexes increases down the series Fe (64 cm^{-1}) < Ru (132 cm^{-1}) < Os (204 cm^{-1}), suggesting that the difference in π-acidity between CO and CS ligands is more fully realized as the π-basicity of the central metal increases.

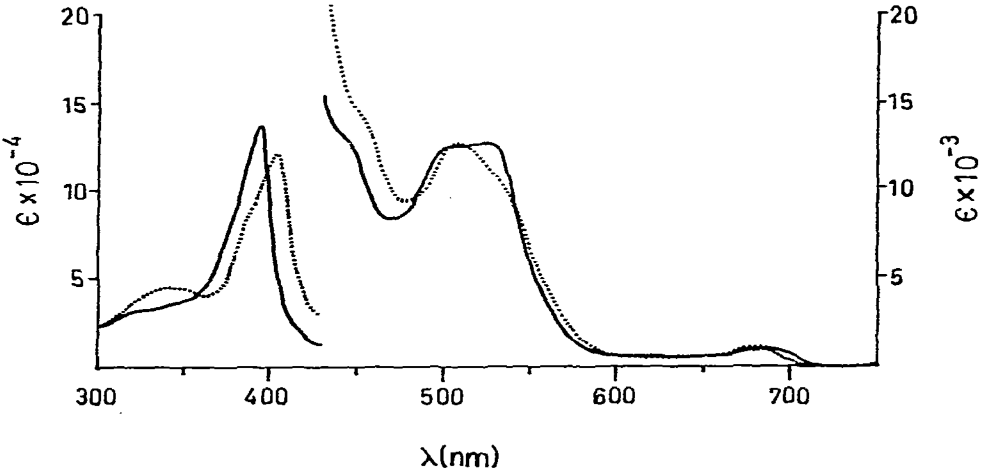


Fig. 2. Absorption spectra of $[NBu_4][Ru(OEP)(CN)_2]$ (V, · · · · · ·) and Ru(OEP)(CN)(Py) (VI, ———) in CH_2Cl_2.

TABLE 3

ELECTRONIC ABSORPTION MAXIMA OF SOME RUTHENIUM COMPLEXES IN CH_2Cl_2

Complex	λ_{max}(log ϵ)
Ru(OEP)CS(Py), I	396(5.29), 518(4.21), 552(4.44)
Ru(OEP)CO(Py), IV	394(5.45), 516(4.22), 548(4.41)
$[NBu_4][Ru(OEP)(CN)_2]$, V	404(5.05), 508(4.06), 680(3.05)
Ru(OEP)CN(Py), VI	395(5.13), 528(4.08), 692(3.09)
$[Ru(OEP)CO(CN)]^-$ [a]	402(5.46), 523(4.07), 554(3.99)

[a] Recorded in CH_2Cl_2/MeOH (1/3 V/V); the Soret band of IV appears at 391 nm in this mixed solvent.

The absorption spectra of the mono- and di-cyano ruthenium(III) complexes VI and V are similar to those of $[Ru(OEP)L_2]^+$, where L = Py, 4-MePy, *N*-methylimidazole [19,23]; in addition to the broad absorption at 500—520 nm, the compounds show weak absorptions in the 600—700 nm region that can be attributed to a porphyrin $\pi \rightarrow$ metal $d(\pi)$ charge-transfer transition (Fig. 2). Complexes V and VI exhibit μ_{eff} values of about 2 BM, as determined by the Evan's method [25], which is consistent with a low spin d^5 configuration [20].

The thiocarbonyl derivative (I) is diamagnetic, and shows the typical ^1H NMR OEP resonances at δ = 1.93 ppm (t, —CH_3), 4.08 ppm (q, —CH_2—), and 10.04 ppm (s, =CH—) in $CDCl_3$ relative to internal TMS. Resonances for the coordinated pyridine occur at 0.90, 4.96, and 5.86 ppm. All these signals have been shifted downfield relative to the corresponding carbonyl complex (IV), where δ(OEP) = 1.90(t), 4.01(q), 9.28(s), and δ(Py) = 0.87, 4.90, 5.80 [19]. This is presumably indicative of overall deshielding due to the electron-withdrawing capacity of the thiocarbonyl ligand. A similar effect is observed between the osmium carbonyl (IX) and thiocarbonyl (III) analogs [6].

Infrared stretching frequencies are found at ν(CO) = 1940 cm^{-1} in IV and ν(CS) = 1283 cm^{-1} in I. A comparison of the ν(CO) and ν(CS) values for the Fe, Ru and Os complexes M(OEP)CS(Py) are listed below:

M	ν(CO)(cm^{-1})	ν(CS)(cm^{-1})	Ref.
Fe	1967	1282	6,23
Ru	1940	1283	this work
Os	1902	1284	6

On comparison with the ν(CO) values, which decrease as expected within the iron triad, the ν(CS) values are insensitive to the metal. The frequencies are higher than that attributed to matrix-trapped CS at 1274 cm^{-1} [26], and are not explicable in terms of the usual π-backbonding arguments; the thiocarbonyl absorption is not pure "CS" and is likely appreciably mixed with ν(M—C(S)) [2,3].

The monocyano complex VI shows a weak vibration for ν(CN) at 2092 cm^{-1} and the dicyano complex V exhibits a slightly stronger peak at ν(CN) = 2098 cm^{-1}. All of the carbonyl, thiocarbonyl and cyano pyridine adducts show a weak absorption at ~1610 cm^{-1} corresponding to the in plane ν(C=C) of coordinated pyridine.

TABLE 4

ELECTROCHEMICAL DATA FOR RUTHENIUM COMPLEXES [a]

Complex	$E^{1}_{1/2}$	$E^{2}_{1/2}$	$E^{3}_{1/2}$
Ru(OEP)CS(Py), I	—	+0.85 [c]	+1.55 [d]
Ru(OEP)CO(Py), IV	—	+0.76 [c]	+1.46 [d]
$[NBu_4][Ru(OEP)(CN)_2]$, V	—0.61 [b]	+0.69 [e]	+1.57 [f]
Ru(OEP)CN(Py), VI	—0.33 [b]	+0.98 [e]	+1.68 [f]

[a] All potentials in Volts vs. Ag/AgCl at 25°C; data in 0.1 *M* NBu_4PF_6 in CH_2Cl_2. [b] Corresponds to $Ru^{III}(OEP) + e^- \rightleftharpoons Ru^{II}(OEP)$. [c] Corresponds to $Ru^{II}(OEP^+) + e^- \rightleftharpoons Ru^{II}(OEP)$. [d] Corresponds to either $Ru^{II}(OEP^{2+}) + e^- \rightleftharpoons Ru^{II}(OEP^+)$, or $Ru^{III}(OEP^+) + e^- \rightleftharpoons Ru^{II}(OEP^+)$. [e] Correspond to $Ru^{III}(OEP^+) + e^- \rightleftharpoons Ru^{III}(OEP)$. [f] Corresponds to either $Ru^{III}(OEP^{2+}) + e^- \rightleftharpoons Ru^{III}(OEP^+)$, or $Ru^{IV}(OEP^+) + e^- \rightleftharpoons Ru^{III}(OEP^+)$.

The redox properties of the ruthenium complexes I, IV, V and VI, as measured by cyclic voltammetry, are listed in Table 4. The voltammograms were recorded under identical experimental conditions. From a comparison of peak heights and ΔE_P of the oxidation and reduction waves, all observed redox processes in the cyclic voltammograms were reversible.

The mono- and di-cyano ruthenium(III) complexes VI and V, show redox waves at $E^{1}_{1/2}$ — 0.33 V and —0.61 V, respectively. The cyanide ligand tends to stabilize the higher valency state and therefore the reduction potentials for $Ru^{III} \rightarrow Ru^{II}$ are much lower than for the bis(amine) or bis(phosphine) systems [17,18,27,28]; as expected, the reduction of V is more difficult than reduction of VI. The second redox wave ($E^{2}_{1/2}$, Table 4) of V and VI, as well as the first wave for the carbonyl (IV) and thiocarbonyl (I) ($E^{2}_{1/2}$, Table 4), is assigned to oxidation of the porphyrin ring; the presence of the CO (or CS) axial ligand raises the potential into the region of porphyrin oxidation [17,27]. The porphyrin ring is slightly more stable toward oxidation in the thiocarbonyl than in the carbonyl, which is again consistent with the greater π-acidity of the CS ligand. Conversely, it is easier to oxidize the porphyrin ring in the anionic species V than in the neutral species VI. There is some ambiguity about the nature of the E^3 wave, since oxidation could involve the metal, or the porphyrin ring again; a similar problem has been encountered previously at similar potentials for both porphyrin [18,27] and phthalocyanine systems [17].

Conclusions

An alternative to photochemical substitution of CO in Ru(OEP)CO(Py), and presumably other Ru(porphyrin)CO(L) systems, involves oxidative decarbonylation using bromine in the presence of cyanide to give cyanoruthenium(III) species. Reduction of these under appropriate conditions yields substituted compounds such as $Ru(OEP)(Py)_2$ and Ru(OEP)CS(Py).

The greater strength of the metal—carbon bond in the thiocarbonyl complexes relative to carbonyl, M(OEP)CS(Py) (M = Fe, Ru, Os) is reflected in the fragmentation patterns observed in the mass spectra of these compounds.

The bathochromic shift in the electronic absorption spectra of the thiocarbonyl complexes relative to the carbonyl derivatives for a given metal is attributed to the greater π-acidity of the CS ligand. This effect increases along the series Fe < Ru < Os, as the extent of metal to ligand backbonding increases. The greater electron withdrawing capacity of the CS ligand relative to CO is also indicated by the systematic differences in the ^{1}H-NMR spectra and from the redox potentials as determined by cyclic voltammetry.

In conclusion, the cyanide ligand has been proved to be useful in the synthesis of neutral, substitution-inert ruthenium(III) complexes, which in turn can be used as starting material for reductive substitution syntheses. The resulting synthesis of the thiocarbonyl compound Ru(OEP)CS(Py) completes the series M(OEP)CS(Py) for the iron triad and confirms the greater π-acidity of the CS ligand relative to CO. This property should be useful as a probe into the nature of ligand—metal—porphyrin π-interactions.

Experimental

Mass spectra were recorded on a KRATOS-AEI MS 902, source temp. 220—240°C, direct insertion probe, electron energy 70 eV.

The electronic absorption spectra were recorded on a Cary 17D spectrophotometer. 100 MHz FT-^{1}H NMR spectra were measured with a Varian XL-100, in $CDCl_3$ unless otherwise indicated. A Perkin Elmer 457 grating infrared spectrophotometer provided the infrared spectra. Cyclic voltammograms were recorded using the apparatus described elsewhere [17].

All solvents used were reagent grade and were dried, distilled and stored under argon before use. Unless indicated otherwise, all reactions were carried out under purified argon using Schlenk techniques. Thiophosgene was purchased from Aldrich Chemical Co.

Tetra-n-butylammonium (dicyano)octaethylphorphinatoruthenate(III), [NBu$_4$][Ru(OEP)(CN)$_2$], V

Complex IV, Ru(OEP)CO(Py) [22] (113 mg, 0.15 mmol), was dissolved in CH_2Cl_2/MeOH (30 ml, 1/1). A solution of KCN (100 mg, 1.54 mmol) in 1.5 ml H_2O was then added dropwise to the porphyrin solution. With constant stirring, 0.6 ml of a Br_2/CH_2Cl_2 solution (0.05 ml Br_2 in 1 ml CH_2Cl_2) was then added dropwise. At this point a thin layer chromatogram (SiO_2/CH_2Cl_2) showed complete conversion of the starting material. The reaction solution was then evaporated to dryness and the residue redissolved in 5% methanol in CH_2Cl_2 and chromatographed on SiO_2 using the methanol/CH_2Cl_2 mixture as eluent. After removal of a small amount of unidentified material, the product was eluted with 25% MeOH in CH_2Cl_2 as a dark orange band. After evaporation to dryness, the product was redissolved in 10 ml CH_2Cl_2, and the solution mixed with 10 ml MeOH containing 100 mg NBu_4Br. Aqueous 0.2 *M* KCN solution (0.5 ml) was then added and the volume reduced to 3 ml by boiling. The large, red-orange plates that formed on cooling were washed several times with 25% aqueous methanol and dried at 80°C/10^{-4} Torr for 12 h. Yield 97 mg (67%). Anal. Found: C, 69.5; H, 8.7; N, 10.4. $C_{54}H_{80}N_7Ru$, calcd.: C, 69.87; H, 8.69; N, 10.56%.

(Cyano)(pyridine)octaethylporphinatoruthenium(III), Ru(OEP)CN(Py), VI

The dicyano anion Ru(OEP)$(CN)_2^-$ was prepared according to the above procedure except that after chromatography the residue was dissolved in 10 ml MeOH to which 1 ml of 1.0 *M* HCl was then added. The solution was then evaporated to dryness and the residue redissolved in 5 ml pyridine. After removing excess pyridine, the residue was eluted with 5% MeOH in CH_2Cl_2 and recrystallized from 7 ml CH_2Cl_2, 7 ml MeOH, 0.05 ml pyridine. After drying at 60° C/10^{-4} Torr for 12 h, 75 mg (73%) of blue black needles were obtained. Anal. Found: C, 68.1; H, 6.9; N, 11.3. $C_{42}H_{49}N_6Ru$, calcd.: C, 68.27. H, 6.68; N, 11.37%.

(Thiocarbonyl)(pyridine)octaethylporphinatoruthenium(II), Ru(OEP)CS(Py), I

Complex VI (53 mg, 0.07 mmol) was dissolved in 10 ml THF under argon. Sodium amalgam (0.2 ml of a 1% solution) was added while vigorously stirring the solution. After the addition of 0.05 ml $CSCl_2$ (caution: stench), the solution changed from orange to reddish pink. Absorption spectra show that the reaction was complete after about 45 min; longer reaction times led to decomposition. Pyridine (0.1 ml) was added, the mixture filtered, and the filtrate evaporated to dryness. The residue was dissolved in CH_2Cl_2 and chromatographed on SiO_2/CH_2Cl_2. The product fraction was recrystallized from 5 ml CH_2Cl_2, 5 ml MeOH, and 0.05 ml pyridine to give blue black crystals. Filtering, washing with MeOH and drying at 60° C/10^{-4} Torr for 12 h, gave 23 mg (43%) of product. Anal. Found: C, 66.6; H, 6.3; N, 9.3. $C_{42}H_{49}N_5S$ Ru, calcd.: C, 66.64; H, 6.52; N, 9.25%.

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