Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Synthesis, Characterization, and Electrochemistry of Novel Diruthenium Cofacial Porphyrin Dimers

James P. Collman,* Kimoon Kim, and Charles R. Leidner†

Received August 28, 1986

Novel diruthenium cofacial porphyrin dimers (FTF4, DPA, and DPB) were synthesized and characterized. Treatment of the dicarbonyl complex of each diporphyrin with triphenylphosphine yielded a five-coordinate bis(triphenylphosphine) complex that has vacant coordination sites inside the diporphyrin cavity. These bis(phosphine) complexes reacted with hydrazine to form μ-hydrazine complexes. Photolysis of the dicarbonyl complexes of DPA and DPB in pyridine produced a tetrakis(pyridine) complex but resulted in a monocarbonyl-bis(pyridine) complex in the case of FTF4. Pyrolysis of the tetrakis(pyridine) complex of DPB yielded a paramagnetic complex containing an intramolecular Ru-Ru bond, which reacted with triphenylphosphine to form the bis(triphenylphosphine) complex. With one exception, electrochemistry of the bis(phosphine) and tetrakis(pyridine) complexes revealed stepwise metal-centered oxidations, indicating strong interaction between the two redox centers.

Introduction

The importance of developing efficient catalysts for multielectron reduction of O_2 or N_2 has been well-recognized. Such catalysts are essential to the design of the oxygen cathode of an air-powered fuel cell and to the electrochemical reduction of dinitrogen.

In 1977, we first described[1] our approach to this problem, which involved the "face-to-face" (FTF) porphyrin dimer, a structure that holds two metal centers in close proximity so that they can act jointly in the coordination and reduction of the substrate. The success of this approach was first demonstrated[2] with the dicobalt derivative of FTF4 (see Figure 1), which catalyzes the direct four-electron reduction of O_2 without producing significant amounts of H_2O_2. Recently, Chang and co-workers reported[3] that dicobalt derivatives of cofacial diporphyrins held by a rigid aromatic spacer (DPA or DPB; see Figure 1) are also efficient four-electron catalysts for O_2 reduction.

In principle this face-to-face diporphyrin approach can be extended to address the problem of the reduction of dinitrogen. Our initial target was the synthesis of a mixed-metal cofacial porphyrin dimer in which one porphyrin ring contains a metal known to bind dinitrogen (Os(II)[4] or Ru(II)[5]) and the other ring a metal that can serve as a Lewis acid (Al(III) or Ti(IV)). The premise is that dinitrogen will be bound by two metals inside the diporphyrin cavity in a "push-pull" manner—one metal acting as a π-electron donor to dinitrogen and the other as a σ- or π-electron acceptor. It is well-established that such a push-pull binding of dinitrogen weakens the N-N bond.[6] However, the difficulty in synthesizing the heterodinuclear dimers led us to study the homodinuclear complexes of ruthenium and osmium first.

To date, all the known synthetic methods for the insertion of ruthenium and osmium into porphyrins yield M(II) (M = Ru, Os) carbonyl complexes which are inactive toward the binding of other π acids such as O_2 and N_2. In light of this obstacle our first target was the synthesis of a diruthenium cofacial porphyrin dimer in which each ruthenium atom has a vacant coordination site inside the porphyrin cavity and has ligands other than CO on the outside. Here we report the synthesis and characterization of novel diruthenium cofacial diporphyrins, including bis(triphenylphosphine) complexes, which have vacant coordination sites inside the cavity as well as a compound containing an intramolecular Ru-Ru bond. The electrochemistry of some of the compounds is also presented.

Experimental Section

UV-visible spectra were recorded on a Cary Model 219 spectrophotometer. IR spectra were measured either on a Nicolet 7199 FTIR spectrometer or on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were obtained either on a 300-MHz Nicolet NMC-300 spectrometer or on a 400-MHz Varian XL-400 spectrometer. Mass spectral analyses were performed either at the Middle Atlantic Mass Spectrometry Laboratory at the School of Medicine Johns Hopkins University, or at Bio-organic, Biomedical Mass Spectrometry Resource at the University of California, San Francisco, CA. Elemental analyses were carried out by Chemical Analytical Services in Berkeley, CA. All manipulations of air-sensitive materials were performed in an inert-atmosphere glovebox (Vacuum Atmospheres Co.) with an oxygen level of less than 2 ppm. Electrochemical experiments were carried out with standard three-electrode cells and instrumentation on approximately 10^{-3} M solutions of the samples in 0.2 M Bu_4NClO_4 in CH_2Cl_2. Spectroelectrochemical experiments were performed on a Hewlett-Packard HP8450A UV-visible spectrometer with an optically transparent, thin-layer electrode[7] comprised of a 2000 lines/in. gold minigrid.

Reagents and Solvents. All solvents and reagents were of reagent grade and were used without further purification except as noted below. All solvents used in the inert-atmosphere box were purified by standard procedures.[8] 2-Methoxyethanol was dried over 3-Å molecular sieves. Dodecacarbonyltriruthenium (Strem Chemical) was recrystallized from hexane. Triphenylphosphine was recrystallized twice from ethanol. ^{15}N-labeled anhydrous hydrazine was prepared from ^{15}N-labeled hydrazine sulfate (90% enriched, Cambridge Isotope Laboratories) as described in the literature.[9] NMR solvents C_6D_6 and CD_2Cl_2 were vacuum-transferred from sodium benzophenone ketyl and P_2O_5, respectively. Pyridine-d_5 was dried over 4-Å molecular sieves.

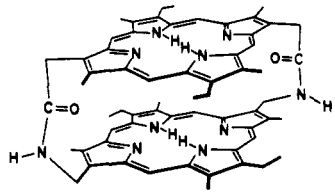
The free-base cofacial porphyrin dimers H_4FTF4,[2,10] H_4DPA,[11] and H_4DPB[12] were prepared as described in the literature with some modifications.

$Ru_2DPA(CO)_2(MeOH)_2$ (1a). To boiling 2-methoxyethanol (25 mL) under nitrogen were added H_4DPA (32 mg) and dodecacarbonyltriruthenium (67 mg), and the reaction mixture was heated at reflux for 5 h. The solvent was removed under reduced pressure, and the residue was chromatographed (silica, 2.5 × 20 cm column, toluene). The first band (5% CH_2Cl_2 in toluene) was collected, evaporated to dryness, and crystallized from CH_2Cl_2/MeOH: yield 28 mg (70%); UV-vis (C_6H_6) λ_{max} (log ϵ) 392 (5.33), 5.20 (4.27), 551 (4.57) nm; IR (KBr) ν_{CO} 1935 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.17 (s, 2 H, meso), 8.95 (s, 5 H, meso and 10-anth), 8.51 (d, J = 8.7 Hz, 2 H, 2,7-anth), 7.76 (t, J = 8.1

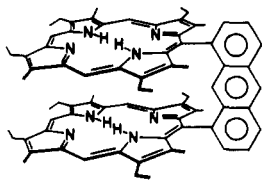
† Present address: Department of Chemistry, Purdue University, West Lafayette, IN 47907.

(1) Collman, J. P.; Elliott, C. M.; Halbert, T. R.; Tovrog, B. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 18.
(2) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.
(3) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725.
(4) Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 741.
(5) (a) James, B. R.; Addison, A. W.; Cairns, M.; Dolphin, D.; Farrell, N. P.; Paulson, D. R.; Walker, S. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 751. (b) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137.
(6) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
(7) Heinemann, W. R.; Norris, B. J.; Goel, J. F. *Anal. Chem.* **1975**, *47*, 79.
(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1966.
(9) Friedrichs, F. *J. Am. Chem. Soc.* **1913**, *35*, 244.
(10) Collman, J. P.; Anson, F. C.; Barnes, C. E.; Bencosme, C. S.; Geiger, T.; Evitt, E. R.; Kreh, R. P.; Meier, K.; Pettman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 2644.
(11) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388.
(12) (a) Chang, C. K.; Abdalmuhdi, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 164. (b) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177.

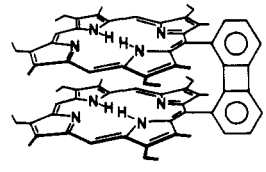
0020-1669/87/1326-1152$01.50/0



H_4FTF4



H_4DPA



H_4DPB

Figure 1. Structures of the cofacial porphyrin dimers employed in this study.

Hz, 2 H, 3,6-anth), 4.10 (m, 4 H, Et), 3.90 (m, 4 H, Et), 3.58 (m, 4 H, Et), 3.38 (s, 12 H, Me), 1.74 (t, J = 7.5 Hz, 12 H, Et), 1.70 (s, 12 H, Me), 1.38 (t, J = 7.2 Hz, 12 H, Et); MS (SIM) m/e 1386 ([M-2MeOH]$^+$). Anal. Calcd for $C_{82}H_{86}N_8O_4Ru_2$: C, 67.93; H, 5.98; N, 7.73. Found: C, 67.86; H, 6.07; N, 7.75.

$Ru_2DPB(CO)_2(MeOH)_2$ (2a). This compound was prepared from H_4DPB (31 mg) in the same manner as the DPA analogue (**1a**) but required longer reaction time (20 h): yield 29 mg (74%); UV–vis (toluene) λ_{max} (log ϵ) 390 (5.38), 519 (4.27), 551 (4.40) nm; IR (KBr) ν_{CO} 1935 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (s, 2 H, meso), 8.55 (s, 4 H, meso), 7.14 (d, J = 7.2 Hz, 2 H, 2,7-biph), 6.95 (t, J = 7.6 Hz, 2 H, 3,6-biph), 6.71 (d, J = 8.0 Hz, 2 H, 4,5-biph), 4.05 (m, 4 H, Et), 3.80 (m, 8 H, Et), 3.54 (m, 4 H, Et), 3.27 (s, 12 H, Me), 2.88 (s, 12 H, Me), 1.64 (t, J = 7.6 Hz, 12 H, Et), 1.40 (t, J = 7.6 Hz, 12 H, Et); MS (SIM) m/e 1359 ([M-2MeOH]$^+$), 1303 ([M − 2CO − 2MeOH]$^+$). Anal. Calcd for $C_{80}H_{84}N_8O_4Ru_3$: C, 67.49; H, 5.95; N, 7.87. Found: C, 67.93; H, 5.68; N, 7.96.

$Ru_2FTF4(CO)_2$ (3a). Free-base FTF4 was metalated by using the procedure employed for the DPA analogue (**1a**). Flash chromatography (silica, 5% EtOH in CH_2Cl_2) of the reaction mixture gave a product that changed its nature slowly on prolonged storage in solution. The freshly prepared compound was used for preparation of $Ru_2FTF4(CO)_2py$ (**3a′**) and of $Ru_2FTF4(PPh_3)_2$ (**3b**) without further purification: yield 68%; UV–vis λ_{max} (CH_2Cl_2) 383 (Soret), 520, 557 nm; IR (CH_2Cl_2) ν_{CO} 2024 (impurity), 1926, 1894 [$\nu_{^{13}CO}$ 2020 (impurity), 1887, 1840], ν_{amide} 1666 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.96 (s, 2 H, meso), 8.89 (s, 2 H, meso), 8.79 (s, 2 H, meso), 6.30 (d, 2 H, NH), 6.02 (dd, 2 H, CH_2), 5.32 (d, 2 H, CH_2), 4.72 (2d, 4 H, CH_2), 4.0–3.6 (m, 8 H, Et), 3.6–3.3 (6 s, 24 H, Me), 1.66 (t, 12 H, Et); MS (FAB) m/e 1237 (M^+), 1209 ([M − CO]$^+$).

$Ru_2FTF4(CO)_2py$ (3a′). This compound was prepared by recrystallizing $Ru_2FTF4(CO)_2$ (**3a**) from CH_2Cl_2/MeOH containing a small amount of pyridine or, more conveniently, by treating the crude metalation product, **3a**, with pyridine and purifying by chromatography (silica, 20% CH_3CN in CH_2Cl_2). The NMR spectrum indicated that the product was a mixture (ca. 2.5:1) of two isomers, which could not be separated by chromatography. The ^{13}C-labeled compound was prepared by stirring the CH_2Cl_2 solution of the compound under ^{13}CO (99%, MSD) overnight: UV–vis (CH_2Cl_2) λ_{max} 385 (Soret), 522, 550 (sh), 557 nm; IR (KBr) ν_{CO} 1926, 1891 ($\nu_{^{13}CO}$ 1877, 1849), ν_{amide} 1667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz; isomer A, major) δ 9.10 (s, 2 H, meso), 8.89 (s, 2 H, meso), 8.84 (s, 2 H, meso); 5.97 (dd, 2 H, CH_2), 5.29 (d, 2 H, CH_2), 5.10 (d, 2 H, NH), 4.93 (d, 2 H, CH_2), 4.64 (d, 2 H, CH_2); 4.0–3.6 (m, Et), 3.5–3.25 (5 s, Me), 1.56 (t, Et), 1.46 (t, Et), 5.50 (t, 1 H, 4-py), 4.48 (t, 2 H, 3,5-py), −0.10 (d, 2 H, 2,6-py); ^{1}H NMR ($CDCl_3$, 300 MHz; isomer B, minor) δ 9.13 (s, 2 H, meso), 8.98 (s, 2 H, meso), 8.95 (s, 2 H, meso), 8.75 (s, 2 H, NH), 4.97 (d, 2 H, CH_2), 4.67 (d, 2 H, CH_2), 4.0–3.5 (m, Et), 3.5–3.25 (5 s, Me), 1.56 (t, Et), 1.46 (t, Et), 5.58 (t, 1 H, 4-py), 4.56 (t, 2 H, 3,5-py), 0.40 (d, 2 H, 2,6-py); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 183.6 (CO), 177.1 (CO); MS (FAB) m/e 1237 ([M − py]$^+$), 1209 ([M − py − CO]$^+$), 1181 ([M − py − 2CO]$^+$). Anal. Calcd for $C_{69}H_{67}O_4Ru_2$: C, 62.95; H, 5.13; N, 11.7. Found: C, 61.41; H, 5.17; N, 11.17.

$Ru_2DPA(PPh_3)_2$ (1b). $Ru_2DPA(CO)_2(MeOH)_2$ (**1a**, 33 mg) was suspended in refluxing toluene (20 mL) in the drybox, and triphenylphosphine (44 mg) was added. The reaction was monitored by UV–vis spectroscopy. After 8 days heating was stopped and the solution was passed down a short alumina (neutral, activity I) column with toluene as the eluent and evaporated to dryness. The unreacted triphenylphosphine was sublimed under high vacuum (5×10^{-6} torr) at 50 °C, leaving an air-sensitive solid that contained a minor impurity (triphenylphosphine oxide): yield 35 mg (81%); UV–vis (toluene) λ_{max} 402 (Soret), 502, 527 nm; IR (CH_2Cl_2) no absorption in the CO stretching region; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 9.01 (s, 1 H, 10-anth), 8.85 (s, 2 H, meso), 8.44 (d, J = 8.7 Hz, 2 H, 2,7-anth), 8.32 (s, 1 H, 9-anth), 7.45 (t, 2 H, 3,6-anth), 7.30 (b, impurity), 6.57 (t, J = 7.2 Hz, 6 H, p-PPh_3), 6.18 (t, J = 7.2 Hz, 12 H, m-PPh_3) 3.69 (t, J = 8.7 Hz, 12 H, o-PPh_3), 3.55–3.20 (m, 16 H, Et), 2.95 (s, 12 H, Me), 1.75 (s, 12 H, Me), 1.49 (t, J = 7.5 Hz, 12 H, Et), 1.12 (t, J = 7.2 Hz, 12 H, Et); MS (SIM) m/e 1855 ([M + H]$^+$).

$Ru_2DPB(PPh_3)_2$ (2b). This compound was prepared from $Ru_2DPB(CO)_2(MeOH)_2$ (**2a**) in the same manner as for the DPA analogue (**1b**): yield 80%; UV–vis (toluene) λ_{max} 360 (sh), 390 (Soret), 514 (sh), 533 nm; IR (CH_2Cl_2) no absorption in the CO stretching region; ^{1}H NMR (C_6D_6, 300 MHz) δ 8.86 (s, 2 H, meso), 7.89 (s, 4 H, meso), 6.94 (d, J = 6.9 Hz, 2 H, 2,7-biph), 6.76 (t, J = 7.2 Hz, 2 H, 3,6-biph), 6.33 (d, J = 7.8 Hz, 2 H, 4,5-biph), 6.16 (t, J = 7.0 Hz, 6 H, p-PPh_3), 5.87 (t, 12 H, m-PPh_3), 4.08 (m, 4 H, Et), 3.72 (m, 4 H, Et), 3.40 (t, J = 9.0 Hz, 12 H, o-PPh_3), 3.32 (m, 8 H, Et), 3.00 (s, 12 H, Me), 2.99 (s, 12 H, Me), 1.73 (t, J = 7.5 Hz, 12 H, Et), 1.40 (t, J = 7.2 Hz, 12 H, Et); MS (SIM) m/e 1829 ([M + H]$^+$). Anal. Calcd for $C_{112}H_{106}N_8P_2Ru_2$: C, 73.58; H, 5.84; N, 6.13. Found: C, 73.82; H, 5.81; N, 6.01.

$Ru_2FTF4(PPh_3)_2$ (3b). This compound was prepared from $Ru_2FTF4(CO)_2$ (**3a**) (16 mg) in a manner similar to that for the DPA analogue (**1b**). The air-sensitive product was further purified by chromatography (alumina (neutral, activity I), 1% EtOH in toluene) in the drybox. The NMR spectrum showed a significant amount (ca. 10%) of triphenylphosphine oxide as a major impurity: yield 15 mg (70%); UV–vis (CH_2Cl_2) λ_{max} 391 (Soret), 506 (sh), 528 nm; IR (CH_2Cl_2) no significant absorption in CO stretching region except a weak broad absorption centered at 1930 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 8.34 (s, 2 H, meso), 8.28 (s, 2 H, meso), 8.12 (s, 2 H, meso), 7.7–7.0 (b, impurity), 6.39 (t, 6 H, p-PPh_3), 6.26 (b, 2 H, NH), 5.94 (q, 12 H, m-PPh_3), 5.74 (q, 2 H, bridge CH_2), 5.00 (d, 2 H, bridge CH_2), 4.35 (s, 4 H, bridge CH_2), 3.75 (m, 4 H, Et), 3.62 (m, 4 H, Et), 3.30 (s, 6 H, Me), 3.23 (s, 12 H, Me), 3.20 (s, 6 H, Me), 3.10 (m, 12 H, o-PPh_3), 1.64 (t, 6 H, Et), 1.57 (t, 6 H, Et); MS (FAB) m/e 1705 (M^+).

$Ru_2DPA(PPh_3)_2(\mu\text{-}NH_2NH_2)$ (1c). In toluene (2 mL) was dissolved $Ru_2DPA(PPh_3)_2$ (**1b**) (10 mg) in the drybox, and 2 drops of anhydrous hydrazine (Sigma) were added. The resulting solution was stirred for 5 h at room temperature and then passed down a short alumina column (neutral, activity I) and evaporated to dryness. The product was further dried under high vacuum: yield 8 mg (81%); UV–vis (toluene) λ_{max} 403 (Soret), 503, 529 nm; ^{1}H NMR (C_6D_6, 300 MHz) δ 8.69 (d, 2 H, meso), 8.62 (s, 1 H, 10-anth), 8.36 (s, 4 H, meso), 8.28 (d, 2 H, 2,7-anth), 7.56 (t, 2 H, 3,6-anth), 7.10 (s, impurity), 6.31 (t, J = 6.6 Hz, 6 H, p-PPh_3), 6.06 (t, J = 6.9 Hz, 12 H, m-PPh_3), 4.00 (m, 4 H, Et), 3.86 (t, J = 8.4 Hz, 12 H, o-PPh_3), 3.68 (m, 4 H, Et), 3.43 (m, 12 H, Et), 1.85 (t, J = 7.5 Hz, 12 H, Et), 1.78 (s, 12 H, Me), 1.45 (t, J = 7.5 Hz, 12 H, Et), −11.29 (s, 4 H, NH); MS (SIM) m/e 1885 ([M + H]$^+$). Anal. Calcd for $C_{114}H_{112}N_{10}P_2Ru_2$: C, 72.59; H, 5.98; N, 7.43. Found: C, 73.21; H, 6.19; N, 7.07.

$Ru_2DPB(PPh_3)_2(\mu\text{-}NH_2NH_2)$ (2c). This complex was prepared from $Ru_2DPB(PPh_3)_2$ (**2b**) in the same manner as for the DPA analogue (**1c**). The ^{15}N-labeled compound was prepared by using anhydrous $^{15}N_2H_4$ (90 atom % enriched): yield 90%; UV–vis (toluene) λ_{max} 403 (Soret), 504, 528 nm; ^{1}H NMR (C_6D_6, 300 MHz) δ 8.42 (s, 2 H, meso), 8.38 (s, 4 H, meso), 6.99 (d, J = 6.6 Hz, 2 H, 4,5-biph), 6.84 (t, 2 H, 3,6-biph), 6.76 (d, 2 H, 2,7-biph), 6.27 (t, J = 7.2 Hz, 6 H, p-PPh_3), 6.02 (t, J = 7.5 Hz, 12 H, m-PPh_3), 3.77 (t, J = 8.4 Hz, 12 H, o-PPh_3), 3.70 (m, 4 H, Et), 3.50 (m, 12 H, Et), 3.10 (s, 12 H, Me), 3.03 (s, 12 H, Me), 1.68 (t, J = 7.5 Hz, 12 H, Et), 1.56 (t, J = 7.5 Hz, 12 H, Et), −11.64 (s, 4 H, NH); ^{1}H NMR ($^{15}N_2H_4$ complex, C_6D_6, 300 MHz) δ −11.64 (d, J_{N-H} = 71.4 Hz, 4 H); MS (SIM) m/e 1862 ([M + H]$^+$). Anal. Calcd for $C_{112}H_{110}N_{10}P_2Ru_2$: C, 72.31; H, 5.96; N, 7.53. Found: C, 72.08; H, 5.91; N, 7.40.

$Ru_2FTF4(PPh_3)_2(\mu\text{-}NH_2NH_2)$ (3c). This compound was prepared from $Ru_2FTF4(PPh_3)_2$ (**3b**) in a manner similar to that for the DPA analogue (**1c**): UV–vis (CH_2Cl_2) λ_{max} 389 (Soret), 401 (sh), 525, 529 nm; IR (CH_2Cl_2): spectrum almost identical with that of **3b**; ^{1}H NMR (CD_2Cl_2) δ 8.20 (s, 2 H, meso), 8.19 (s, 2 H, meso), 8.15 (s, 2 H, meso), 8.14 (s, 2 H, meso), 7.7–7.1 (m, b, impurity), 6.45 (t, J = 7.2 Hz, 6 H, p-PPh_3), 6.03 (m, 12 H, m-PPh_3), 5.76 (b, 2 H, bridge NH), 5.54 (dd, 2 H, bridge CH_2), 5.18 (dd, 2 H, bridge CH_2), 4.52 (d, J = 16 Hz, bridge CH_2), 4.35 (d, J = 16 Hz, bridge CH_2), 3.55–3.24 (m, 20 H, o-PPh_3 and Et), 3.18 (s, 6 H, Me), 3.04 (s, 6 H, Me), 1.50 (t, 12 H, Et), −12.53 (b,

4 H, N_2H_4); MS (FAB) *m/e* 1738 (M^+).

$Ru_2DPA(py)_4$ (1d). A solution of $Ru_2DPA(CO)_2(MeOH)_2$ (**1a**, 9 mg) in pyridine (10 mL) was placed in a 25-mL Pyrex flask equipped with a Teflon vacuum stopcock and degassed by three freeze–pump–thaw cycles. The solution was irradiated with a medium-pressure mercury lamp for 46 h and then evaporated to dryness. The residue was taken up with THF, and the solution was passed down a short alumina column (neutral, activity I) and evaporated to dryness: yield 8 mg (78%); UV–vis (benzene) λ_{max} (log ϵ) 366 (sh), 390 (sh), 398 (5.35), 414 (sh), 499 (4.48), 525 (4.76) nm; IR (CH_2Cl_2) no absorption in CO stretching region; ^1H NMR (C_6D_6) δ 10.58 (s, 1 H, 10-anth), 9.37 (s, 2 H, meso), 9.14 (s, 4 H, meso), 8.93 (s, 1 H, 9-anth), 8.32 (d, J = 8.8 Hz, 2 H, 2,7-anth), 7.36 (t, J = 8.0 Hz, 2 H, 3,6-anth), 7.04 (d, J = 6.8 Hz, 2 H, 4,5-anth), 4.76 (t, J = 7.2 Hz, 2 H, 4-py1), 4.12 (t, J = 6.8 Hz, 4 H, 3,5-py1), 3.75–3.35 (m, 16 H, Et), 3.30 (t, J = 7.6 Hz, 2 H, 4-py2), 2.96 (s, 12 H, Me), 2.52 (t, J = 7.6 Hz, 4 H, 3,5-py2), 2.49 (s, 12 H, Me), 2.21 (d, J = 5.2 Hz, 4 H, 2,6-py1), 1.67 (t, J = 7.2 Hz, 12 H, Me), 1.43 (b, 12 H, Me), 1.35 (d, J = 5.6 Hz, 4 H, 2,6-py2); MS (SIM): *m/e* 1647 ($[M + H]^+$), 1569, 1489, 1410, 1329. Anal. Calcd for $C_{98}H_{98}N_{12}Ru_2$: C, 71.51; H, 6.00; N, 10.21. Found: C, 71.36; H, 6.11; N, 9.97.

$Ru_2DPB(py)_4$ (2d). This compound was prepared from $Ru_2DPB(CO)_2(MeOH)_2$ (**2a**, 11 mg) in the same manner as for the DPA analogue (**1d**): yield 10 mg (80%); UV–vis (THF) λ_{max} (log ϵ) 364 (sh), 390 (sh), 396 (5.30), 410 (sh), 454 (4.49), 499 (4.52), 526 (4.81) nm; IR (CH_2Cl_2) no absorption in CO stretching region; ^1H NMR (C_6D_6) δ 9.39 (s, 2 H, meso), 9.17 (s, 4 H, meso), 6.99 (d, J = 6.8 Hz, 2 H, 2,7-biph), 6.64 (t, J = 8.0 Hz, 3,6-biph), 6.33 (d, J = 8.8 Hz, 4,5-biph), 4.71 (t, J = 7.2 Hz, 2 H, 4-py1), 4.08 (t, J = 7.2 Hz, 4 H, 3,5-py1), 3.9–3.5 (m, 16 H, Et), 3.69 (s, 12 H, Me), 3.28 (t, J = 7.6 Hz, 2 H, 4-py2), 2.98 (s, 12 H, Me), 2.43 (t, J = 6.8 Hz, 4 H, 3,5-py2), 2.09 (d, J = 5.2 Hz, 4 H, 2,6-py1), 1.68 (t, J = 7.6 Hz, 12 H, Et), 1.59 (b, 12 H, Et), 1.39 (d, J = 5.6 Hz, 4 H, 2,6-py2); MS (SIM) *m/e* 1620 (M^+), 1541, 1462, 1383, 1304. Anal. Calcd for $C_{96}H_{96}N_{12}Ru_2$: C, 71.17; H, 5.97; N, 10.38. Found: C, 71.28; H, 5.90; N, 10.09.

$Ru_2FTF4(CO)(py)_2$ (3d). A solution of $Ru_2FTF4(CO)_2py$ (**3a'**, 18 mg) in pyridine (20 mL) in a quartz vessel was irradiated with a medium-pressure mercury lamp for 46 h while being flushed continuously with a stream of Ar. The solution was evaporated to dryness and chromatographed (alumina (neutral, activity I), 10% CH_3CN in THF) in the drybox. The NMR spectrum indicated the product was a mixture (ca. 1:1) of two isomers, each of which contains two coordinated pyridines: yield 14 mg (75%); UV–vis (THF) λ_{max} 387 (Soret), 522, 558 nm; IR (CH_2Cl_2) ν_{CO} 1901 ($\nu_{^{13}CO}$ 1856 cm^{-1}), ν_{amide} 1663 cm^{-1}; ^1H NMR (pyridine-d_5, 300 MHz) δ, 9.63 (s, 2 H, meso), 9.39 (s, 2 H, meso), 9.18 (s, 2 H, meso), 9.12 (s, 4 H, meso), 8.88 (s, 2 H, meso), 8.65 (s, 2 H, meso), 8.10 (b, 2 H, NH_A), 7.98 (b, 2 H, NH_B), 6.34 (dd, 2 H, $(CH_2)_A$), 6.08 (dd, 2 H, $(CH_2)_B$), 5.72 (dd, 4 H, $(CH_2)_{A,B}$), 5.30 (d, 2 H, $(CH_2)_A$), 5.13 (d, 2 H, $(CH_2)_B$), 4.96 (d, 2 H, $(CH_2)_A$), 4.80 (d, 2 H, $(CH_2)_B$), 4.0–3.6 (m, 16 H, $Et_{A,B}$), 3.6–3.0 (8 s, 48 H, $Me_{A,B}$), 1.45 (t, 12 H, $Et_{A,B}$); ^1H NMR (CD_2Cl_2, coordinated pyridines) δ 5.65 (t, 1 H, $(4\text{-py})_{A1}$), 5.56 (t, 1 H, $(4\text{-py})_{B1}$), 4.62 (t, 2 H, $(3,5\text{-py})_{A1}$), 4.51 (t, 2 H, $(3,5\text{-py})_{B1}$), 4.32 (br t, 2 H $(3,5\text{-py})_{A2}$), 4.18 (br t, 2 H, $(3,5\text{-py})_{B2}$), 0.62 (br t, 2 H, $(2,6\text{-py})_{A2}$), 0.36 (d, 2 H, $(2,6\text{-py})_{A1}$), 0.22 (d, b, 2 H, $(2,6\text{-py})_{B2}$), −0.13 (d, 2 H, $(2,6\text{-py})_{B1}$); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 177.5 (CO), 177.2 (CO).

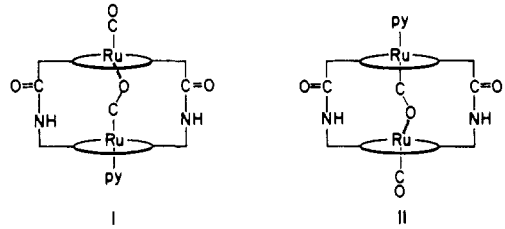
Ru_2DPB (2e). A solution of **2d** (5 mg) in benzene (1 mL) was lyophilized. The resulting amorphous solid was heated at 230 °C under high vacuum (5×10^{-6} torr) for 12 h to give a dark green air-sensitive compound in quantitative yield: UV–vis (C_6D_6) λ_{max} (log ϵ) 375 (4.90), 508 (3.97), 630 (3.59), 734 (3.56) nm; ^1H NMR (C_6D_6, 400 MHz) δ 31.54 (s, 12 H, Me); 29.89 (s, 2 H, Me), 24.58 (m, 4 H, CH_2), 22.66 (m, 4 H, CH_2), 20.34 (s, 4 H, meso), 18.71 (s, 2 H, meso), 12.16 (m, 4 H, CH_2), 10.56 (m, 4 H, CH_2), 7.84 (dd, 2 H, biph), 7.47 (2 d, 4 H, biph), 3.70 (t, 12 H, CH_3), 3.31 (t, 12 H, CH_3); MS (CI) *m/e* 1303 ($[M - H]^-$).

Results and Discussion

The structure of the cofacial porphyrin dimers used in this study are shown in Figure 1.

Diruthenium Dicarbonyl Complexes. Ruthenium was inserted into free-base cofacial porphyrin dimers by a modification of the literature method.[13] The resulting diruthenium compounds were isolated as dicarbonyl complexes, **1a–3a**, analogously to monomeric ruthenium porphyrins.

The FTF4 complex **3a** is unstable and changes its nature slowly on prolonged storage in solution. Treatment of **3a** with pyridine, however, yields a stable compound (**3a'**), which has been formulated as $Ru_2FTF4(CO)_2py$ on the basis of spectroscopic and mass spectral data. The ^1H NMR spectrum indicates that **3a'** is a mixture of two isomers (ca. 2.5:1), each of which contains one coordinated pyridine molecule. The IR spectrum of **3a'** shows equally intense carbonyl stretching absorptions at 1926 and 1891 cm^{-1}, which are shifted to 1877 and 1849 cm^{-1} on ^{13}CO substitution, in addition to the strong amide band at 1667 cm^{-1}. The carbonyl stretching frequency of Ru(OEP)(CO)py (OEP = octaethylporphyrin dianion) was reported to be 1925 cm^{-1}.[14] The ^{13}C NMR spectrum of **3a'** (^{13}CO exchanged) exhibits two equally intense signals at 183.6 and 177.1 ppm, compared to 183 ppm for Ru(OEP)(^{13}CO)THF.[15] These IR and NMR data suggest that coordinated CO occupies two different sites in **3a'**, one inside and the other outside the diporphyrin cavity. We propose that **3a'** is a mixture of isomers I and II.



The DPA and DPB complexes **1a** and **2a**, crystallized from CH_2Cl_2/MeOH, show a single CO stretching absorption at ~1930 cm^{-1}. The ^1H NMR spectra indicate the presence of a single isomer in each case. The orientation of the two carbonyl ligands has not been rigorously established, but we believe them to occupy the binding sites outside the diporphyrin cavity on the basis of their chromatographic behavior and the CO stretching frequencies.

Triphenylphosphine Complexes. The formation of bis(triphenylphosphine) complexes of monomeric ruthenium porphyrins upon treatment of the carbonyl precursors with excess triphenylphosphine has been well established.[16–18] Under similar conditions the dicarbonyl complexes **1a–3a** were slowly converted to the extremely air-sensitive diamagnetic bis(triphenylphosphine) complexes **1b–3b**, respectively. The triphenylphosphine ligands apparently bind only on the outside of the diporphyrin cavity (presumably due to their size), thereby leaving a vacant coordination site on each Ru inside the cavity. The ^1H NMR spectrum of **2b**, shown in Figure 2A, is consistent with this structure. Five-coordinate Ru(OEP)PPh_3 has been observed[18] spectroscopically in a dilute solution of Ru(OEP)$(PPh_3)_2$ and isolated[19] in impure form from the reaction of Ru(OEP)(PPh_3)Br with zinc amalgam. Compound **2b** is the first example of an analytically pure five-coordinate ruthenium porphyrin. The coordinatively unsaturated bis(triphenylphosphine) complexes in solution react with O_2 instantly and irreversibly, as evidenced by UV–vis spectra. The fate of the complexes in this process was not studied, but the decrease in the Soret band intensity and the broad absorption band above 600 nm suggest[20] the formation of π-cation-radical complexes.

There is no evidence indicating that the five-coordinate bis(phosphine) complexes **1b–3b** bind dinitrogen or substituted acetylenes. The π acidity of triphenylphosphine may be responsible for the inertness of the complexes toward these substrates. The reaction chemistry of these complexes with other substrates is currently under investigation.

Bridging Hydrazine Complexes. The bis(phosphine) complexes

(13) Tsutsui, M.; Ostfeld, D.; Hoffman, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 1820.

(14) Buchler, J. W.; Kokisch, W.; Smith, P. D. *Struct. Bonding (Berlin)* **1978**, *34*, 79.
(15) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1976**, *15*, 134.
(16) Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1971**, *1*, 57.
(17) Boschi, T.; Bontempelli, G.; Mazzocchin, G. A. *Inorg. Chim. Acta* **1979**, *37*, 155.
(18) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.
(19) James, B. R.; Mikkelsen, S. R.; Leung, T. W.; Williams, G. M.; Wong, R. *Inorg. Chim. Acta* **1984**, *85*, 209.
(20) Führhop, J.-H. *Struct. Bonding (Berlin)* **1974**, *18*, 1.

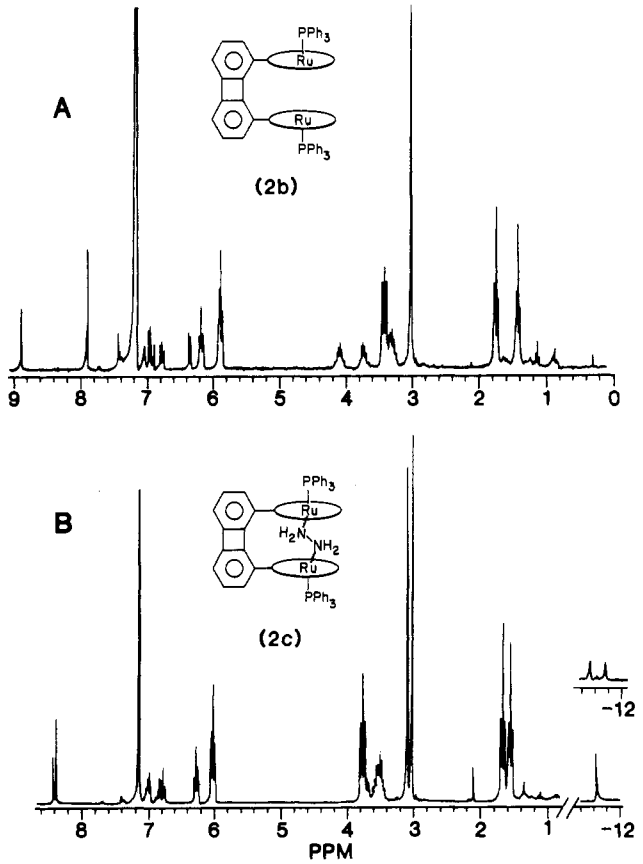
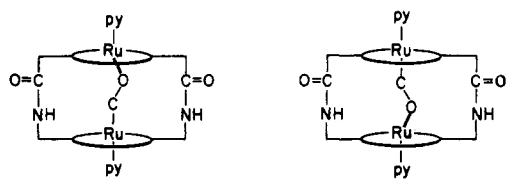


Figure 2. ^1H NMR spectra (C_6D_6, 300 MHz) of (A) $Ru_2DPB(PPh_3)_2$ (**2b**) and (B) $Ru_2DPB(PPh_3)_2(\mu\text{-}N_2H_4)$ (**2c**).

1b–3b react with anhydrous hydrazine under N_2 to give the complexes **1c–3c**, respectively, in which a hydrazine ligand bridges two Ru centers presumably in an η^1,η^1 fashion. The bound hydrazines in these complexes show ^1H NMR signals in the region of ~−11 to −12 ppm. Such a dramatic shift to higher field supports the assignment of a bridging hydrazine inside the diporphyrin cavity. Figure 2B shows the NMR spectrum for complex **2c**. Use of ^{15}N-labeled (90% enriched) hydrazine causes a split in the ^1H NMR signal due to ^{15}N–^1H coupling, as shown in the inset of Figure 2B. The bridging hydrazine complexes are fairly stable toward O_2 but are eventually oxidized irreversibly on prolonged exposure to air.

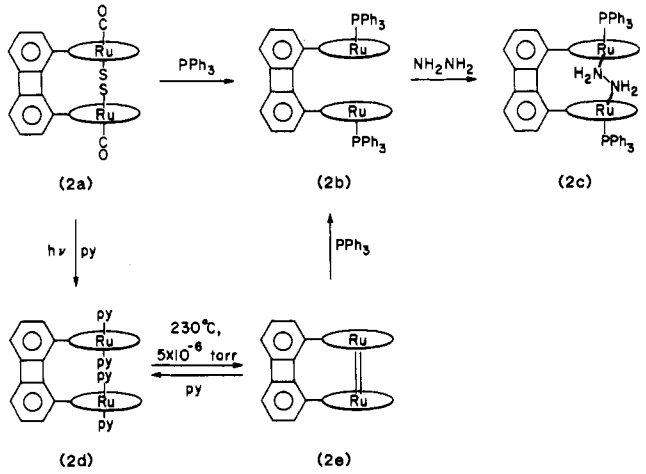
Photolysis. On photolysis, ruthenium carbonyl porphyrins have been found to lose CO to produce bis(solvato) complexes.[21] Photolysis of **3a** or **3a′** in pyridine under similar conditions afforded the compound **3d**. The ^1H NMR spectrum of **3d** indicates the presence of two isomers, each of which contains two coordinated pyridines per diporphyrin. A strong absorption at 1901 cm^{-1} in the IR spectrum and signals at ~177 ppm in the ^{13}C NMR spectrum were observed, suggesting the existence of a CO ligand inside the diporphyrin cavity. When CO is bubbled through the dichloromethane solution of **3d**, its precursor **3a** and 1 equiv of free pyridine are generated, as indicated by ^1H NMR. We therefore propose structures III and IV as the components of the **3d** mixture.



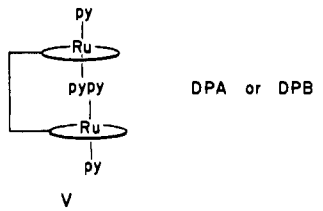
III IV

(21) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.

Scheme I



In contrast to the case for the amide-bridged diporphyrin, photolysis of **1a** and **2a** in pyridine removes both CO ligands to yield air-stable tetrakis(pyridine) complexes **1d** and **2d**, respectively. The ^1H NMR spectra of both **1d** and **2d** show two sets of equally intense signals due to four pyridine ligands per molecule. One set of pyridine resonances is very close to those of monomeric $Ru(OEP)(py)_2$;[22] the other set is shifted upfield by 0.7–1.65 ppm. We therefore propose the structure V, with two pyridines inside and two outside the diporphyrin cavity.



V

To make room for the "inside" pyridine ligands, the two porphyrin planes must be displaced laterally and/or the cavity must be "opened" by increasing the bite angle of diporphyrin. The crystal structures of Ni_2DPA and Cu_2DPB show that two parallel porphyrin rings slip with respect to each other.[23] Presumably the FTF4 structure, having two connecting bridges, is more rigid and therefore is not able to accommodate large ligands inside the cavity.

Pyrolysis. We previously reported that the solid-state pyrolysis of ruthenium bis(pyridine) porphyrins leads to the formation of ruthenium porphyrin dimers joined by multiple metal–metal bonds.[22,24] Vacuum pyrolysis of the tetrakis(pyridine) complex **2d** yields Ru_2DPB (**2e**), which contains an intramolecular Ru–Ru double bond. The UV–vis and NMR spectra of this paramagnetic compound are similar to those of $[Ru(OEP)]_2$. A preliminary report of the synthesis and characterization of **2e** has been published.[25] The complex **2e** reacts immediately with pyridine to give first an intermediate complex, which then slowly (~24 h) converts to the tetrakis(pyridine) complex **2d**. We propose this intermediate to be $Ru_2DPB(py)_2$ with both pyridines bound outside. Triphenylphosphine reacts instantly with **2e** to provide the bis(phosphine) adduct **2b**.

Under similar pyrolysis conditions the DPA analogue **1d** gave an insoluble black material, which was partially converted back to the tetrakis(pyridine) complex **1d** on prolonged treatment with pyridine. We believe the insoluble material to be a polymer linked

(22) Collman, J. P.; Barnes, C. E.; Sweptson, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.
(23) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417.
(24) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030.
(25) Collman, J. P.; Kim, K.; Garner, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1711.

Table I. Half-Wave Potentials (V vs. Ag Wire)[a] for Oxidation and Reductions of Diruthenium DPA and DPB Complexes

compds	$E_{1/2}$, V [n][b] oxidn ligand	oxidn metal	red ligands
$Ru_2DPA(PPh_3)_2$ (**1b**)	1.01 [2], 0.84 [2]	0.06 [2]	
$Ru_2DPB(PPh_3)_2$ (**2b**)	1.07 [2]	0.23 [1], −0.06 [1]	
$Ru_2DPA(PPh_3)_2(\mu\text{-}N_2H_4)$ (**1c**)	1.18[c] [2] (irrev)	0.28 [1], −0.01 [1]	
$Ru_2DPB(PPh_3)_2(\mu\text{-}N_2H_4)$ (**2c**)	1.04 [2]	0.21 [1], −0.09 [1]	
$Ru_2DPA(py)_4$ (**1d**)	1.24 [1], 1.19 [1]	0.12 [1], 0.01 [1]	−1.88[d] [2] (irrev)
$Ru_2DPB(py)_4$ (**2d**)	1.24 [2]	0.14 [1], 0.03 [1]	−1.85[d] [2] (irrev)

[a] $E_{1/2}$(ferrocene/ferrocenium) = 0.39 ± 0.02 V vs. Ag wire. [b] Number of electrons involved in redox process. [c] Anodic peak potential. [d] Cathodic peak potential.

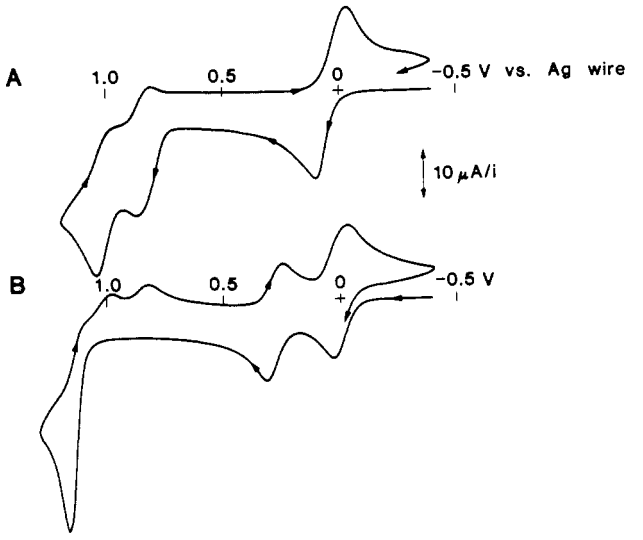


Figure 3. Cyclic voltammograms of (A) 0.3 mM $Ru_2DPA(PPh_3)_2$ (**1b**) and (B) 0.4 mM $Ru_2DPA(PPh_3)_2$ in 0.2 M Bu_4NClO_4/CH_2Cl_2 (scan rate 100 mV/s).

by intermolecular Ru–Ru bonds. Presumably the distance between two metal centers in DPA is too long (~1 Å longer than in DPB)[23] to accommodate an intramolecular Ru–Ru bond.

The preparation and substitution chemistry of the diruthenium(II) DPB complexes are summarized in Scheme I. Diruthenium DPA complexes transform similarly with the exception of the pyrolysis resulting in a polymer as mentioned above.

Electrochemistry. The redox properties of DPA and DPB complexes were studied by using cyclic and rotated-disk voltammetry in 0.2 M Bu_4NClO_4 in CH_2Cl_2. The half-wave potentials ($E_{1/2}$) for each redox couple obtained from cyclic voltammetry are listed in Table I. The cyclic voltammetric responses of $Ru_2DPA(PPh_3)_2$ (**1b**) and of the corresponding hydrazine complex **1c** are shown in Figure 3.

The data in Table I indicate that two reversible one-electron-redox couples occur between −0.1 and +0.3 V (vs. Ag wire) for all the compounds except $RuDPA(PPh_3)_2$ (**1b**), which exhibits a reversible 2e couple instead. Rotating-disk voltammetry indicates these are all oxidations. Further oxidation(s) occurs above 0.8 V in each compound. From a comparison to the published electrochemistry of $Ru(OEP)(py)_2$[26] and $Ru(OEP)(PBu_3)_2$[27] we assign the oxidations between −0.1 and +0.3 V for each compound

(26) Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5937.
(27) Barley, M.; Becker, J. Y.; Domazetis, G.; Dolphin, D.; James, B. R. *Can. J. Chem.* **1983**, *61*, 2389.

Table II. UV–Visible Spectral Data of Electrogenerated Complexes

compds	oxidn states	λ_{max}, nm
$Ru_2DPA(PPh_3)_2(\mu\text{-}N_2H_4)$ (**1c**)	Ru(II), Ru(III)	395 (Soret), 502, 506
	Ru(III), Ru(III)	387 (Soret), 508, 540 (sh)
$Ru_2DPB(PPh_3)_2$ (**2b**)	Ru(II), Ru(III)	381 (Soret), 498 (sh), 518
	Ru(III), Ru(III)	380 (Soret), 518
$Ru_2DPB(PPh_3)_2(\mu\text{-}N_2H_4)$ (**2c**)	Ru(II), Ru(III)	360 (sh), 394 (Soret), 502, 526
	Ru(III), Ru(III)	388 (Soret), 516, 542 (sh)
$Ru_2DPB(py)_4$ (**2d**)	Ru(III), Ru(III)	388 (Soret), 506, 537

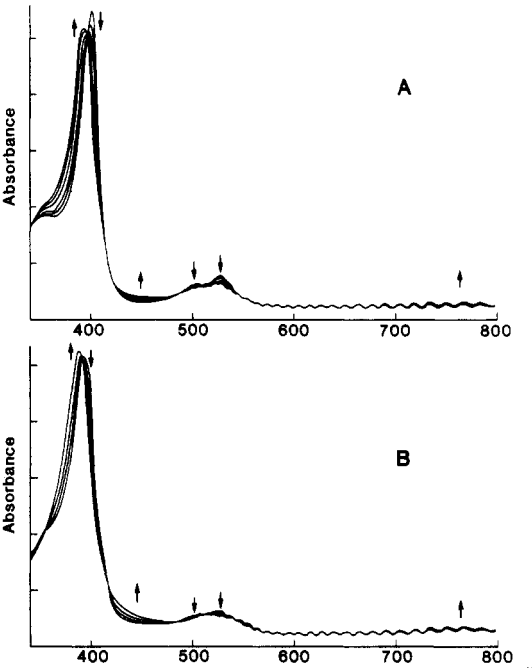


Figure 4. UV–visible spectra of $Ru_2DPB(PPh_3)_2(\mu\text{-}N_2H_4)$ (**2c**) taken at an optically transparent thin-layer electrode (A) during the first oxidation at 0.05 V (vs. Ag wire) and (B) during the second oxidation at 0.5 V (vs. Ag wire).

to be metal-centered and the ones at higher potential to be ligand oxidations. The tetrakis(pyridine) complexes **1d** and **2d** show an irreversible reduction at ~−1.9 V, which we believe occurs on the ligands. No reduction waves are found for other complexes within the negative-potential limit of the solvent.

The two ruthenium centers are oxidized stepwise in all these compounds except $Ru_2DPA(PPh_3)_2$ (**1b**), in which two metals are oxidized simultaneously (Figure 3A). This presumably indicates only a weak metal–metal interaction due to large unmediated space between two metal centers in this DPA complex. However, once a hydrazine molecule bridges two Ru metals of the DPA complex, the two redox centers interact with each other, resulting in two well-separated oxidations (Figure 3B).[28] In contrast, the metal-centered oxidation wave of $Ru_2DPB(PPh_3)_2$ is split by 0.3 V, indicating a strong through-space interaction between the two metal centers.

Controlled-potential electrolysis was carried out in bulk and/or thin-layer cells, and the products of the oxidation were monitored by UV–vis spectra. Table II summarizes the spectral data of electronic absorption of the complexes generated by electrolysis. For **1c**, **2b**, and **2c**, the two metal-centered oxidations are so well separated (~0.3 V) that stable mixed-valence (Ru(II)Ru(III)) complexes can be generated (the disproportionation constant is $\sim 10^{-5}$). Figure 4 illustrates the UV–vis spectral change of the

(28) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.

hydrazine complex (**2c**) during the controlled-potential electrolysis in a thin-layer cell. During oxidation at 0.05 V (vs. Ag wire) an isosbestic spectral change was observed, which we believe corresponds to the change from Ru(II)Ru(II) to Ru(II)Ru(III) (Figure 4A). The Soret band decreases in intensity slightly and shifts toward the blue. The visible bands, which are partly obscured by an interference pattern of the thin-layer cell, also change position (λ_{max}) and decrease in intensity. When the applied potential was changed to 0.5 V, a similar isosbestic behavior corresponding to the change from Ru(II)Ru(III) to Ru(III)Ru(III) was observed (Figure 4B). The small change in intensity of the Soret peak and the lack of strong absorption above 550 nm in both oxidations support the assignment of metal-centered oxidation.[29] When the applied potential is switched to −0.2 V, these spectral changes are reversed to restore the original spectrum of **2c**. The reversibility of this electrochemical process leads us to believe that the bridging hydrazine remains intact during these metal-centered electrooxidations. A continuous decrease in intensity of the Soret band upon electrolysis above 1.2 V indicates irreversible degradation of the reduction product. The original spectrum of **2c** is not restored when the potential is switched to −0.2 V.

Oxidation of the hydrazine complex **1c** with $AgBF_4$ gave a product showing a UV–vis spectrum identical with that of the Ru(III)Ru(III) species generated by controlled-potential electrolysis of **1c**.

Osmium Complexes. Dicarbonylosmium complexes of DPA and FTF4 analogous to **2a** and **3a′** were synthesized. Photolysis of the $Os_2FTF4(CO)_2$ complex gave a mixture of two isomeric monocarbonyl complexes analogously to **3d**. Attempts to make pure bis(triphenylphosphine)osmium complexes by the same procedure used for the ruthenium analogues failed, apparently because of the much slower substitution kinetics of osmium with respect to those of ruthenium.

Oxidation of the $Os_2DPA(CO)_2$ complex with MCPBA (*m*-chloroperoxybenzoic acid) gave a product that shows a UV–vis spectrum similar to that of $Os(OEP)(O)_2$.[30] The oxidation product, which has not been fully characterized, reacts with hydrazine hydrate to give a compound that has been formulated as $Os_2DPA(NH_3)_4$.[31] An analogous transformation leading to $Os(OEP)(NH_3)_2$ has been reported.[32] Further work on osmium complexes is in progress.

(29) Kadish, K. M.; Davis, D. G.; Führhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1014.
(30) Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 341.

Summary and Conclusion

Novel diruthenium cofacial porphyrin dimers have been synthesized and characterized. Some of these complexes are analogous to known monomeric ruthenium porphyrins (i.e the dicarbonyl and the tetrakis(pyridine) complexes). In addition, we have prepared coordinatively unsaturated bis(triphenylphosphine) complexes in which a bulky phosphine binds each metal on the outside of the cavity, leaving a vacant coordination site on each metal inside. Such structures may serve as catalysts for the electrochemical reduction of dinitrogen. Although the bis(triphenylphosphine) complexes do not bind dinitrogen, they do bind hydrazine, a possible reduction product of dinitrogen, inside the cavity. Electrochemistry reveals strong interaction between two metal centers in these complexes except $Ru_2DPA(PPh_3)_2$ (**1b**), as indicated by well-separated metal-centered oxidation waves in cyclic voltammograms. Vacuum pyrolysis of the tetrakis(pyridine) complex of DPB yields a paramagnetic complex containing an intramolecular Ru–Ru bond, which reacts with triphenylphosphine to give $Ru_2DPB(PPh_3)_2$ (**2b**). This suggests a general route to five-coordinate diruthenium DPB complexes, $Ru_2DPB(L)_2$, where L is a bulky ligand that cannot enter the diporphyrin cavity. With the proper choice of L this type of compound may bind dinitrogen or other small molecules between the two metal centers and serve as a catalyst for subsequent electrochemical transformations.

Acknowledgment. We thank G. T. Yee and M. G. Finn for helpful discussion. The support of the National Science Foundation is gratefully acknowledged (Grant NSFCHE83-18512). We also thank the Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director) supported by NIH Division of Research Resources Grant RR01614.

(31) ^1H NMR (C_6D_6, 300 MHz): δ 8.81 (s, 1 H, anth), 8.63 (s, 1 H, anth), 8.19 (d, 2 H, anth), 7.85 (s, 2 H, meso), 7.80 (d, 2 H, anth), 7.54 (dd, 2 H, anth), 3.64 (q, 8 H, Et), 3.10 (q, 8 H, Et), 3.04 (s, 12 H, Me), 2.15 (s, 12 H, Me), 1.78 (t, 12 H, Et), 1.17 (t, 12 H, Et), −9.42 (s, 6 H, NH_3), −9.70 (s, 6 H, NH_3). UV–vis (THF): λ_{max} 349, 392 (Soret), 474, 484 (sh), 505 nm. MS (SIM): *m/e* 1575 ($[M - 2H]^+$), 1558, 1541, 1524, 1506.
(32) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 198.

Contribution No. 7149 from The Chemical Laboratories, California Institute of Technology, Pasadena, California 91125

Electrochemical Studies of Reactive Polyanionic Chelating Ligand Complexes in Liquid Sulfur Dioxide. Formation of Highly Oxidizing Inorganic Complexes

Fred C. Anson, Terrence J. Collins,*[1] Stephen L. Gipson, John T. Keech, and Terry E. Krafft

Received March 20, 1986

Liquid SO_2 has been used as a medium for testing the limits of oxidative stability of osmium complexes of the polyanionic chelating (PAC) ligand $[\eta^4$-CHBA-DCB$]^{4-}$ (**1**) (H_4CHBA-DCB = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene). The production of potent solution-stable oxidants has resulted. Liquid SO_2 is a very useful solvent for obtaining electrochemical information on highly reactive, oxidizing inorganic complexes that decompose in conventional media.

Introduction

Stable potent one-electron oxidants are rare. The development of new compounds with very positive formal potentials poses several problems. First, new oxidation-resistant ligand complements must be found. Second, the solution media in which powerful oxidants are studied must also be resistant to oxidation. In the process of developing new polyanionic chelating (PAC) ligands (e.g. **1**) that are compatible with highly oxidizing metal centers,[2-7] we have developed a series of stable oxidants (e.g. **2**)

(1) Alfred P. Sloan Research Fellow, 1986–1988; Dreyfus Teacher-Scholar, 1985–1989.

0020-1669/87/1326-1157$01.50/0