the limited size of the basis set: it is well-known that unpolarized double-ζ bases give poorer values for bond angles at atoms with lone pairs than they do for bond lengths.[25] Last, we note the poor value for $r(C{=}O)$ obtained by use of the pseudopotential for Cr instead of the all-electron model. This result, and the similar one obtained for CrO_2F_2, indicates the pseudopotential may have insufficient flexibility to describe the Cr atom core in highly positive environments created by the presence of very electronegative substituents.

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Registry No. $CrO_2(NO_3)_2$, 16017-38-2; Cr, 7440-47-3.

Supplementary Material Available: Tables of total intensities and final backgrounds from each plate and average intensities (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Dihalogenoruthenium(IV)-, Diphenylruthenium(IV)-, and Phenylruthenium(III)-Tetraphenylporphyrin Complexes, Including the Crystal Structure of $Ru(TPP)Br_2$

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The paramagnetic ($S = 1$) $Ru(TPP)X_2$ complexes (X = halide) are made by treatment of $[Ru(TPP)]_2$ with HBr, HCl, or I_2 (TPP = the dianion of 5,10,15,20-tetraphenylporphyrin). The dibromo species (**2**) crystallizes in the tetragonal system, space group C_{4h}^5-$I4/m$, with $a = 13.686$ (9) Å, $c = 9.711$ (7) Å, and $Z = 2$. The structure has been refined on F^2 to final R and R_w values of 0.050 and 0.080, respectively, for 72 variables and 1639 observations; the value of $R(F)$ for the 1354 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ is 0.034. The molecule has imposed symmetry $4/m$. As a consequence, the porphyrin plane is strictly planar; the phenyl rings are perpendicular to this plane, as is the Ru-Br bond. The Ru-Br distance is 2.425 (2) Å, the shortest recorded for any Ru-Br bond. ^1H NMR isotropic shift data are consistent with π-donation from the halide. With PhLi, **2** yields diamagnetic $Ru(TPP)Ph_2$ (**5**), which can be thermally decomposed to Ru(TPP)Ph (**6**); kinetic data imply a stronger Ru-C bond in **5** compared to the corresponding octaethylporphyrin complex (by 2.6 kcal/mol). A light-induced O_2 oxidation of **6** gives diamagnetic $[Ru(TPP)Ph]_2O$.

Introduction

Organometallic chemistry at metalloporphyrin centers is of current interest, and developments in such chemistry of ruthenium porphyrins (excluding the carbonyl complexes) originally stemmed, at least in part, from attempts to model certain aspects of cytochrome P450 systems where Fe-carbon and porphyrin nitrogen-carbon bonded intermediates are implied.[2] Work from this laboratory first reported an entry into Ru(porphyrin)(π-olefin) complexes,[3] and such chemistry involving direct coordination of an olefin (or acetylene) at a Ru(II) porphyrin center has been extended by ourselves,[4] and others.[5,6] A more extensive organoruthenium porphyrin chemistry with derivatives in oxidation states II-IV has been developed via reactions of electrophiles with Ru(0) precursors[5,7] or via treatment of Ru(IV) dihalides or dimeric $[Ru(por)]_2^{2+}$ precursors with Grignard reagents or lithium alkyls/aryls.[2,8-10] Synthesized $Ru(por)R_2$ and Ru(por)R species (R = aryl, alkyl) themselves have extensive redox chemistry[2,9,11] that enriches further this organometallic area.

The porphyrin ligands utilized in the above reports have been mainly OEP[2,3,7-9,11] and TTP[5,7] and occasionally TMP[4,6] and OCP.[6] The present paper reports on TPP derivatives, in particular the $Ru(TPP)X_2$ complexes where X = Cl, Br, and I (including a structure of the X = Br species), $Ru(TPP)Ph_2$, and Ru(TPP)Ph; in an earlier communication,[11] we noted the existence of such complexes and listed the ^1H NMR data for Ru(TPP)Ph.

Experimental Section

^1H NMR spectra were obtained on a Varian XL 300-MHz or Bruker WH 400-MHz FT spectrometer. UV/visible spectra were recorded on a Perkin-Elmer 552A spectrophotometer, and mass spectra (EI and FAB) were obtained on a Kratos-AEI MS902 instrument; FAB spectra in a *p*-nitrobenzyl alcohol matrix were acquired with a 6-kV ion source, a 7-8-kV, 1-mA xenon gun, and a 10 s/decade scan rate. Elemental analyses were carried out by P. Borda of the Department of Chemistry, UBC. Solution magnetic moment measurements at room temperature were done by the Evans method, using 5-10 mM concentrations of the complexes in $CDCl_3$ with TMS as reference (2% in volume);[12] diamagnetic corrections were made by totaling individual contributions from each atom present with the use of Pascal's constants.[13]

Anhydrous HBr(g) was obtained from Matheson, and technical grade HCl(g) was supplied by BDH Chemical Co; O_2 was obtained from Union Carbide of Canada Ltd. and dried where necessary by passage through an Aquasorb tube (Mallinckrodt); I_2 and PhLi (2.0 M in cyclohexane/diethyl ether, 70/30) were Aldrich products; solvents except benzene and toluene were used directly without further purification; benzene and toluene were refluxed and distilled from CaH_2 and stored over molecular sieves (4 Å) under N_2. Where necessary, the solvent was degassed by three to six freeze-pump-thaw cycles. Ru was obtained on loan from Johnson Matthey Ltd., in the form of $RuCl_3{\cdot}H_2O$ (~40% Ru). The

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(10) Abbreviations used: por = dianion of an unspecified porphyrin; OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TTP, TMP, OCP, and TPP are dianions of the 5,10,15,20-tetrasubstituted porphyrins with *p*-tolyl, mesityl, 2,6-dichlorophenyl, and phenyl groups, respectively; py = pyridine; Cp = η^5-cyclopentadienyl; in NMR spectra, s = singlet, d = doublet, t = triplet, and b = broad; in UV/vis spectra, sh = shoulder.

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free-base porphyrin H_2(TPP) was synthesized by a literature method.[14]

Ruthenium Complexes. $Ru_3(CO)_{12}$,[15] Ru(TPP)(CO)L (L = vacant, EtOH, THF),[16] $Ru(TPP)(py)_2$,[17,18] and $[Ru(TPP)]_2$[18] (**1**) were prepared by literature procedures, and their spectroscopic data (NMR, UV/vis, IR) were in agreement with those reported.

$Ru(TPP)Br_2$ (2). CH_2Cl_2 (10 mL) saturated with HBr was added to **1** (180 mg, 0.13 mmol) via vacuum transfer; to the resulting deep red, air-stable solution was added *n*-hexane (30 mL), which precipitated a dark red solid. This was collected, dissolved in CH_2Cl_2 (10 mL), reprecipitated, and dried in vacuo at 70 °C for 2 days (95% yield). Crystals suitable for an X-ray structure determination were obtained by slow vapor diffusion of *n*-hexane (10 mL) into a $CHCl_3$ solution (5 mL) of **2** (5 mg) at room temperature. Anal. Calcd for $C_{44}H_{28}Br_2N_4Ru$: C, 60.49; H, 3.23; Br, 18.29; N, 6.41. Found: C, 60.29; H, 3.30; Br, 18.11; N, 6.44. $\mu_{eff} = 2.7\ \mu_B$. Mass spectrum (EI) (*m/z* (relative intensity), assignment): 793 (6), 795 (5), $[M - Br]^+$; 714 (34), $[M - 2Br]^+$; 80 (100), 82 (97), $[HBr]^+$. ^1H NMR (δ; $CDCl_3$, room temperature): −47.95 (b s, 8 H, pyrrole β-H), 5.21 (d, 8 H, H_o), 5.82 (t, 4 H, H_p), 12.75 (t, 8 H, H_m). UV/vis (CH_2Cl_2, 25 °C; λ_{max}, nm (log ϵ)): 548 (sh), 517 (4.14), 413 (5.08).

$Ru(TPP)Cl_2$ (3). This species was prepared via the method described above for **2**, but with HCl in place of HBr. Yield: 83%. Anal. Calcd for $C_{44}H_{28}Cl_2N_4Ru$: C, 67.35; H, 3.60; Cl, 9.04; N, 7.14. Found: C, 67.10; H, 3.64; Cl, 8.97; N, 7.10. Mass spectrum (EI) (*m/z* (relative intensity), assignment): 749 (8), $[M - Cl]^+$; 714 (100), $[M - 2Cl]^+$. ^1H NMR (δ; $CDCl_3$, room temperature): −57.72 (b s, 8 H, pyrrole β-H), 6.60 (t, 4 H, H_p), 7.10 (b s, 8 H, H_o), 11.52 (b s, 8 H, H_m). UV/vis (CH_2Cl_2, 25 °C; λ_{max}, nm (log ϵ)): 552 (sh), 514 (4.08), 406 (5.32).

$Ru(TPP)I_2$ (4). To 50 mg of **1** (0.035 mmol) was added a solution of I_2 (20 mg, 0.079 mmol) dissolved in *n*-hexane (30 mL) under N_2, and the resulting suspension was stirred for 3 days at room temperature. The solvent was then removed by vacuum. Attempts at purification by recrystallization or chromatographic procedures were unsuccessful. ^1H NMR of the crude sample (δ; $CDCl_3$, room temperature): −23.10 (8 H, pyrrole β-H), 4.64 (8 H, H_o), 6.14 (4 H, H_p), 12.37 (8 H, H_m)—all broad singlets.

$Ru(TPP)Ph_2$ (5). A solution of **2** (100 mg, 0.11 mmol) in benzene (200 mL) was stirred under N_2 as a 5-fold excess of PhLi solution was added dropwise. After being stirred for 0.5 h, the mixture was washed with H_2O (3 × 100 mL) in air and the organic phase then chromatographed on an alumina I column (3 × 3 cm) with C_6H_6 as eluant. The product was eluted quickly and the solvent removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (10 mL) and reprecipitated by addition of MeOH (20 mL). The dark red crystals collected by filtration were dried for 2 days at 70 °C in vacuo. Yield: 59%. Anal. Calcd for $C_{56}H_{38}N_4Ru$: C, 77.49; H, 4.41; N, 6.45. Found C, 77.11; H, 4.41; N, 6.37. Mass spectrum (EI) (*m/z* (relative intensity), assignment): 867 (1), $[M - H]^+$; 791 (4), $[M - C_6H_5]^+$; 714 (3), $[M - 2C_6H_5]^+$; 78 (100), $[C_6H_6]^+$. ^1H NMR (δ; $CDCl_3$, room temperature): 8.35 (s, 8 H, pyrrole β-H), 8.05 (d, 8 H, H_o), 7.72 (m, 12 H, H_m, H_p): axial phenyl 1.31 (d, 4 H, H_o), 5.22 (t, 4 H, H_m), 5.63 (t, 2 H, H_p). UV/vis (toluene, 25 °C; λ_{max}, nm (log ϵ)): 585 (3.41), 492 (4.14), 418 (5.02), 349 (4.59).

Ru(TPP)Ph (6). To 100 mg of **5** (0.12 mmol) was vacuum-transferred 20 mL of oxygen-free, dried benzene. The mixture was degassed further and then heated at 100 °C for ca. 30 h. Removal of the solvent by vacuum transfer and drying in vacuo at 100 °C for 2 days gave dark red **6** in quantitative yield. Anal. Calcd for $C_{50}H_{33}N_4Ru$: C, 75.93; H, 4.21; N, 7.10. Found: C, 75.67; H, 4.37; N, 7.10. Mass spectrum (EI) (*m/z* (relative intensity), assignment): 791 (100), $[M]^+$; 714 (45), $[M - C_6H_5]^+$; 78 (94), $[C_6H_6]^+$. ^1H NMR (δ; C_6D_6, room temperature): −30.94 (b s, 8 H, pyrrole β-H), 2.65 (d, 1 H, H_o), 4.60 (d, 1 H, $H_{o'}$), 4.47 (t, 1 *H*, H_m), 4.94 (t, 1 H, $H_{m'}$), 5.53 (t, 1 *H*, H_p); axial phenyl −89.53 (b s, 2 H, H_o), −57.47 (b s, 1 H, H_p), 51.65 (b s, 2 H, H_m). UV/vis (toluene, 25 °C; λ_{max}, nm (log ϵ)): 607 (sh), 517 (4.03), 411 (5.08).

Table I. Crystallographic Data for $Ru(TPP)Br_2$[a]

formula	$C_{44}H_{28}Br_2N_4Ru$	T, °C	−150[b]
fw	873.6	density (calcd), g/cm^3	1.595
space group	C_{4h}^5–$I4/m$	linear abs coeff, cm^{-1}	26.34
a, Å	13.686 (9)	transm factors	0.609–0.786[c]
c, Å	9.711 (7)	$R(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.034
V, Å^3	1818.9	$R_w(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.038
Z	2		

[a] Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.7093 Å), graphite monochromator. [b] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. I. de Vic, 31320 Castanet-Tolosan, France. [c] The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018).

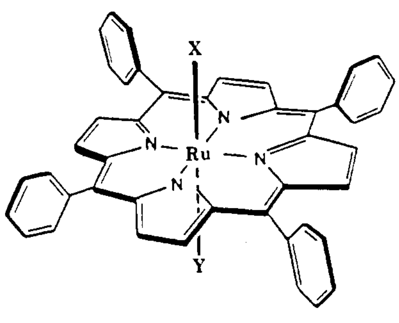
$[Ru(TPP)Ph]_2O$ (7). A benzene solution (20 mL) of **6** (30 mg, 0.038 mmol) was exposed to laboratory light and stirred under 1 atm of O_2 (wet or dried) for 4 days at room temperature. The solution was chromatographed on an alumina I column (3 × 2 cm) with C_6H_6 as eluant, and the product eluted quickly. Removal of the solvent by a rotary evaporator and drying the residue at 70 °C in vacuo for 2 days gave **7** in 66% yield. Anal. Calcd for $C_{100}H_{66}N_8ORu_2$: C, 75.17; H, 4.16; N, 7.01. Found: C, 74.70; H, 4.30; N, 6.68. Mass spectrum (*m/z* (relative intensity), assignment): EI 791 (48), $[Ru(TPP)Ph]^+$; 730 (2), $[Ru(TTP)O]^+$; 714 (100), $[Ru(TPP)]^+$; FAB 1597, $[[Ru(TPP)Ph]_2O - H]^+$. ^1H NMR (δ; $CDCl_3$, room temperature): 8.50 (s, 16 H, pyrrole β-H), 8.82 (d, 8 H, H_o), 7.91 (t, 8 H, H_m), 7.27 (d, 8 H, $H_{o'}$), 7.48 (t, 8 H, $H_{m'}$), 7.60 (t, 8 H, H_p); axial phenyl −1.42 (d, 4 H, H_o), 3.91 (t, 4 H, H_m), 4.54 (t, 2 H, H_p). UV/vis (CH_2Cl_2; λ_{max}, nm: 558, 509, 403(Soret), 366.

X-ray Crystallographic Analysis of $Ru(TPP)Br_2$ (2). Some details of the data collection are given in Table I; others are given in Table SI.[19] The structure was solved by a conventional heavy-atom method,[20] the coordinates of the Ru, N, and Br atoms being determined from the Patterson function and those of the pyrrole rings by difference Fourier methods. Refinement was by full-matrix least-squares methods on F_o^2, use being made of all the data (1639 reflections and 72 variables). Hydrogen atom positions were idealized [C–H = 0.95 Å; $B(H) = B(C) + 1$ Å^2] and not varied. A final difference electron density map was essentially featureless with $\Delta_{\rho_{max}}$ = 1.0 (1) e/Å^3. Analysis of $\sum w\Delta^2$ over ranges of θ, F_o^2, and Miller indices revealed no unusual trends.

Bond lengths and angles are given in Table II, and final positional and equivalent isotropic thermal parameters are given in Table III. Anisotropic thermal parameters and structure amplitudes are included as supplementary material (Tables SII and SIII).[19]

Results and Discussion

The $Ru(TPP)X_2$ Complexes (X = Halide). The dihalide complexes **2** (X = Br) and **3** (X = Cl) are prepared in the same manner as described briefly for the OEP analogues,[8] via the interaction of $[Ru(TPP)]_2$ (**1**) with HX in CH_2Cl_2. We had thought originally that traces of halogen from the HX were responsible for the oxidation process, but an HX:Ru_2 stoichiometry



1: X = Ru(TPP), Y = vacant.
2: X = Y = Br. 3: X = Y = Cl.
4: X = Y = I. 5: X = Y = Ph.
6: X = Ph, Y = vacant.
7: X = Ph, Y = ORu(TPP)Ph.

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(19) Supplementary material.

(20) Programs and methods used are standard: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273.

Table II. Bond Distances (Å) and Angles (deg) in Ru(TPP)Br_2

Ru–Br	2.425 (2)	C(1)–C(2)	1.438 (5)	C(4)–C(5)	1.397 (5)	C(6)–C(7)	1.380 (3)
Ru–N	2.037 (3)	C(4)–C(3)	1.440 (5)	C(1)–C(5′)[a]	1.396 (5)	C(7)–C(8)	1.393 (4)
N–C(1)	1.380 (4)	C(2)–C(3)	1.353 (5)	C(5)–C(6)	1.504 (5)	C(8)–C(9)	1.380 (4)
N–C(4)	1.385 (4)						

C(1)–N–C(4)	106.7 (3)	C(1)–N–Ru	126.9 (2)	C(4)–N–Ru	126.5 (2)
N–C(1)–C(2)	109.3 (3)	N–C(4)–C(3)	109.1 (3)	C(1)–C(2)–C(3)	107.6 (3)
C(4)–C(3)–C(2)	107.4 (3)	N–C(4)–C(5)	125.8 (3)	N–C(1)–C(5′)	125.6 (3)
C(3)–C(4)–C(5)	125.1 (3)	C(4)–C(5)–C(6)	117.1 (3)	C(1′)–C(5)–C(6)	117.6 (3)
C(4)–C(5)–C(1′)	125.3 (3)	C(5)–C(6)–C(7)	120.4 (2)	C(5)–C(6)–C(7′)	120.4 (2)
C(6)–C(7)–C(8)	120.4 (3)	C(7)–C(8)–C(9)	120.2 (3)	C(8)–C(9)–C(8′)	119.5 (3)

[a] Primed atoms are those generated by symmetry.

Table III. Positional Parameters and B_{eq} (Å^2) for Ru(TPP)Br_2

atom	x	y	z	B_{eq}
Ru	0	0	0	0.919 (5)
Br	0	0	0.249667 (48)	1.681 (6)
N(1)	0.03949 (20)	−0.14349 (20)	0	1.05 (5)
C(1)	−0.02222 (25)	−0.22325 (24)	0	1.20 (6)
C(2)	0.03501 (27)	−0.31134 (24)	0	1.36 (6)
C(3)	0.13031 (26)	−0.28506 (25)	0	1.31 (6)
C(4)	0.13390 (24)	−0.17987 (25)	0	1.18 (6)
C(5)	0.21939 (25)	−0.12413 (25)	0	1.24 (6)
C(6)	0.31475 (25)	−0.17876 (25)	0	1.22 (6)
C(7)	0.35886 (20)	−0.20430 (21)	0.12264 (28)	2.06 (5)
C(8)	0.44572 (20)	−0.25737 (21)	0.12276 (31)	2.18 (5)
C(9)	0.48847 (26)	−0.28486 (26)	0	1.50 (6)
H1C(2)	0.0102	−0.3763	0	2.6
H1C(3)	0.1849	−0.3280	0	2.6
H1C(7)	0.3300	−0.1855	0.2074	3.3
H1C(8)	0.4755	−0.2748	0.2076	3.5
H1C(9)	0.5472	−0.3224	0	3.0

of 4:1 has been demonstrated for the Ru(OEP)Br_2 synthesis, eq 1. Although the fate of the "4H" remains to be established, H_2

$$[\mathrm{Ru(OEP)}]_2 + 4\mathrm{HX} \rightarrow 2\mathrm{Ru(OEP)Br_2} + \text{“4H”} \qquad (1)$$

is not formed.[21] Reactions of the $[Ru(por)]_2$ species with Br_2 or Cl_2 can be used for synthesis of Ru(por)X_2, but side products are formed by halogenation of the porphyrin ligand.[8,22] The bis(iodo) complex **4** has been isolated only within a mixture, with I_2 as the oxidant. The syntheses of **2** and **3** from **1** are lengthy and involve the sequence $Ru_3(CO)_{12}$ → Ru(por)(CO) → Ru(por)$(py)_2$ → $[Ru(por)]_2$ → Ru(por)X_2, including a photochemical step for conversion of the carbonyl to the bis(pyridine) species and a high-temperature/-vacuum procedure for removing the pyridines.[16-18] Complex **2** can be formed directly, in situ, from Ru(por)(CO) via Br_2 oxidation to the Ru(II) π cation radical,[16c] followed by decomposition of this at 100 °C, eq 2,[22] but the process is not useful synthetically.[22,23]

$$2\mathrm{Ru(por^{\bullet +})(CO)Br} \rightarrow \mathrm{Ru(por)Br_2} + \mathrm{Ru(por)(CO)} + \mathrm{CO} \qquad (2)$$

Worth mentioning is that the synthesis of the Ru(por)X_2 species according to eq 1 was fortuitous, in that we were attempting to prepare Ru(por)X species for use as precursors with O atom donors in "P450-like monooxygenase" systems for catalytic oxygenation of hydrocarbons. We had demonstrated such activity with Ru(por)Br(PR_3) complexes[24] and considered that a phosphine-free precursor would be more desirable; because we had shown that Ru(III) porphyrin complexes are readily synthesized from a Ru(II) species using O_2 (or air) oxidation in the presence of an acid HX,[25] the same procedure was tested on the $[Ru(por)]_2$ species. The Ru(por)X_2 complexes were formed, and the syntheses were then shown to occur even in the absence of air. Of note, the Ru(por)X complexes have been prepared subsequently by ammoniacal reduction of the Ru(por)X_2 species.[21a]

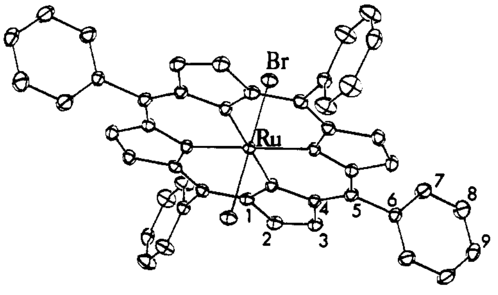

Figure 1. The Ru(TPP)Br_2 structure, showing 50% probability vibrational ellipsoids along with the numbering scheme of the carbon atoms. The molecule has crystallographically imposed symmetry $4/m$ (C_{4h}).

To our knowledge, Ru(TPP)Br_2 (**2**) is the first structurally characterized, paramagnetic Ru(IV) porphyrin complex, its solution magnetic moment corresponding to two unpaired spins (S = 1; a d^4 occupancy of a closely spaced t_{2g} set, with either d_{xy} or $d_{xz,yz}$ being lowest in energy[17,26]). Ruthenium(IV) monooxo porphyrin complexes also have a triplet ground state,[27] while a structure has been reported for an analogous non-porphyrin macrocyclic ligand system.[28]

Complex **2** has crystallographically imposed symmetry $4/m$. As a consequence, the porphyrin ring is strictly planar; the phenyl rings are perpendicular to this plane, as is the Ru–Br bond (Figure 1). With the exception of this Ru–Br bond, the distances and angles in this porphyrin are normal (Table II). The Ru–Br bond length 2.425 (2) Å is short compared to those found in a wide range of Ru(II) and Ru(III) complexes containing a terminal Br atom (2.47–2.57 Å).[25,29] This may be attributed in part to contraction of electron density with the higher oxidation state of

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the metal; reasonably consistent with this are data for Ru(I)–Br bonds (2.60 Å) within $[Ru(CO)_2P^tBu_3]_2(\mu\text{-}Br)_2$[30] (although this is a bridging Br) and relatively short Ru(VI)–Br bonds (2.45 Å) in $[RuBr_4N]^-$.[31] Structural data reported for two apparently diamagnetic Ru(IV) complexes containing terminal bromides give averaged Ru–Br lengths of 2.560 Å within $RuBr_2(Cp)(\eta^3\text{-}C_3Ph_3)$[32] and 2.547 Å within the substituted cyclopentadienyl complex $RuBr_3(C_5Me_4Et)(CO)$ although there was a disorder problem in the "$Br_3(CO)$" unit.[33] These Ru(IV)–Br bond lengths seem reasonable when compared to those reported for some Ru(IV)–Cl bond lengths (2.34–2.46 Å)[34] using the premise that Ru–Br bonds are typically 0.12 Å longer than corresponding Ru–Cl bonds (based on data, however, for Ru(II) and Ru(III) systems);[29c] these reported Ru(IV)–Br bond lengths, however, seem long on consideration of the Ru(II)- and Ru(III)–Br data given above. In any case, the Ru–Br bond length in **2** (the first determined for a paramagnetic Ru(IV) complex) is the shortest yet recorded for *any* Ru–Br bond. There could be significant π-donation from the halides generally in the $Ru(por)X_2$ species (and hence a shortening of the bond), and this could certainly account qualitatively for the paramagnetism of these complexes compared to the diamagnetism of the $Ru(por)R_2$ complexes,[2,8,9] in particular **2** vs $Ru(TPP)Ph_2$ (**5**); **5** must have a $(d_{xz,yz})^4(d_{xy})^0$ ground state, while π-donation would destabilize the $d_{xz,yz}$ set to give the required, more closely spaced, t_{2g} set. A "close approach" of Br to the metal has been suggested also in $Ti(TPP)Br_2$, a d^0 system, where the Ti(IV)–Br bond length (2.454 Å)[35] is similar to that found here for Ru(IV)–Br; of note, the effective ionic radii of Ru(IV), 0.62 Å, and Ti(IV), 0.605 Å, are also essentially the same.[36]

Difference in spin states between **2** and $Ru(OEP)Ph_2$ will not account for the possibly shorter Ru–N bond length in the former (2.037 (3) vs 2.047 (3) Å[21b]), which probably results from the slightly smaller size of the TPP ring versus the OEP ring.[37] The averaged Ru–N length in **2** appears to be the shortest found in all Ru(TPP) complexes reported thus far, including those of Ru(II)[16b,38] and Ru(III)[39] and the dinuclear Ru(IV) species $[Ru(TPP)(p\text{-}MeC_6H_4O)]_2O$.[39]

The $Ru(TPP)X_2$ complexes (**2**–**4**) give well-resolved ^1H NMR spectra with the resonances paramagnetically shifted compared to their positions in diamagnetic Ru(II)–TPP complexes.[17,18] The meso-phenyl resonances, at least in the dibromo species, appear as sharp multiplets, and this is consistent with D_{4h} symmetry and a $d_{xy}{}^2d_{xz}{}^1d_{yz}{}^1$ occupancy, giving rise to an efficient electron relaxation mechanism.[22,40] The large upfield pyrrole isotropic shifts, small upfield shifts for the ortho and para protons, and smaller downfield shifts for the meta protons (e.g. Figure 2) show that π-delocalization dominates the isotropic shifts.[22,41] The trends in the chemical shifts for the pyrrole protons of **2**–**4** (Cl (δ –57.7) > Br (δ –47.95) > I (δ –23.10)) are consistent with transfer of π-spin density from the fully occupied 3e(π) porphyrin MO to the metal $d_{xz,yz}$ orbitals, the extent of transfer decreasing with increasing π-donor ability of the axial halide ligand. The NMR data thus also support the structural data regarding the short Ru–Br bond.

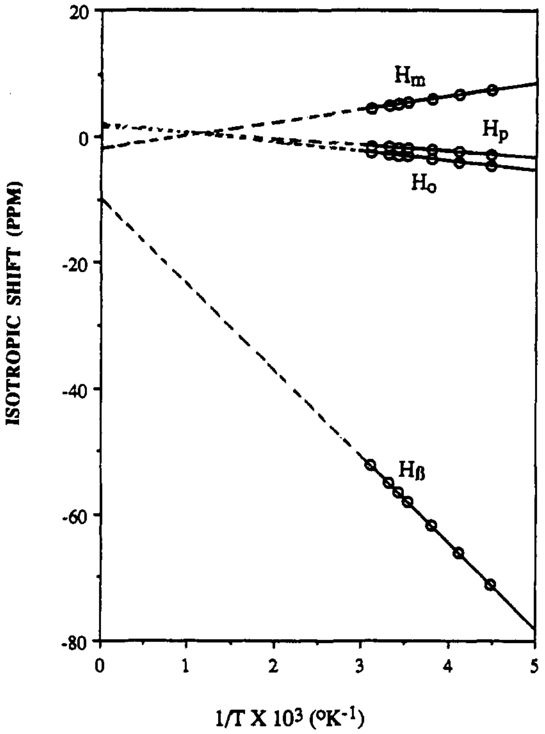

Figure 2. Isotropic shifts vs T^{-1} for $Ru(TPP)Br_2$ in $CDCl_3$. The shifts of $Ru(TPP)(py)_2$ in C_6D_6 were used as a diamagnetic reference (δ): 8.64, H_β; 8.22, H_o; 7.49, H_m and H_p.

The isotropic shifts for **2** conform to Curie behavior and the existence of a single spin state from –50 to +50 °C, the extrapolated intercepts to $T^{-1} = 0$ being close to 0 ppm (Figure 2). A paper by Rachlewicz and Latos-Grazynski,[22] which appeared after completion of the present work on **2**, discusses paramagnetic ^1H NMR shifts of the closely related $Ru(TTP)Br_2$ species (formed in situ); the contact shift sign of the *p*-Me resonance is opposite to that of the H_p proton in **2** (Figure 2), further evidence for a π-delocalization mechanism. These authors, however, favor a metal → porphyrin π-charge-transfer process.

The $Ru(TPP)Br_2$ complex is robust and, for example, does not decompose on refluxing anaerobically in toluene for 24 h.

The $Ru(TPP)Ph_n$ Complexes ($n = 2$ (5) and $n = 1$ (6)). The reaction of **2** with PhLi in benzene readily gives the diamagnetic diphenyl derivative **5**, while anaerobic thermolysis of solutions of **5** affords the paramagnetic (assumed $S = {}^1/_2$)[11] monophenyl complex **6**. The chemistry is entirely analogous to that of the corresponding OEP systems.[8,11] The ^1H NMR, mass spectral, and elemental analytical data are consistent with the assigned formulations.

The axial phenyl protons of **5** shift upfield owing to the ring current effect from the porphyrin plane, the shifts being close to those reported for $Ru(OEP)Ph_2$,[2,8] which has been structurally characterized,[21b] and $Ge(TPP)Ph_2$;[42] the resonances of the TPP ligand are typical for a diamagnetic species.[16b,38,39] The ^1H NMR spectrum of **6** (Figure 3) shows the large paramagnetic shifts of the axial phenyl protons, which are readily assigned by analogy with data for Ru(OEP)Ph[11] and low-spin Fe(TPP)Ph:[43] the large upfield shift of the pyrrole β-H singlet, and smaller upfield shifts (to the 6–2 ppm region) for the TPP phenyl resonances. The doubling pattern of the ortho and meta protons of the TPP phenyl groups results from lack of symmetry in the porphyrin plane

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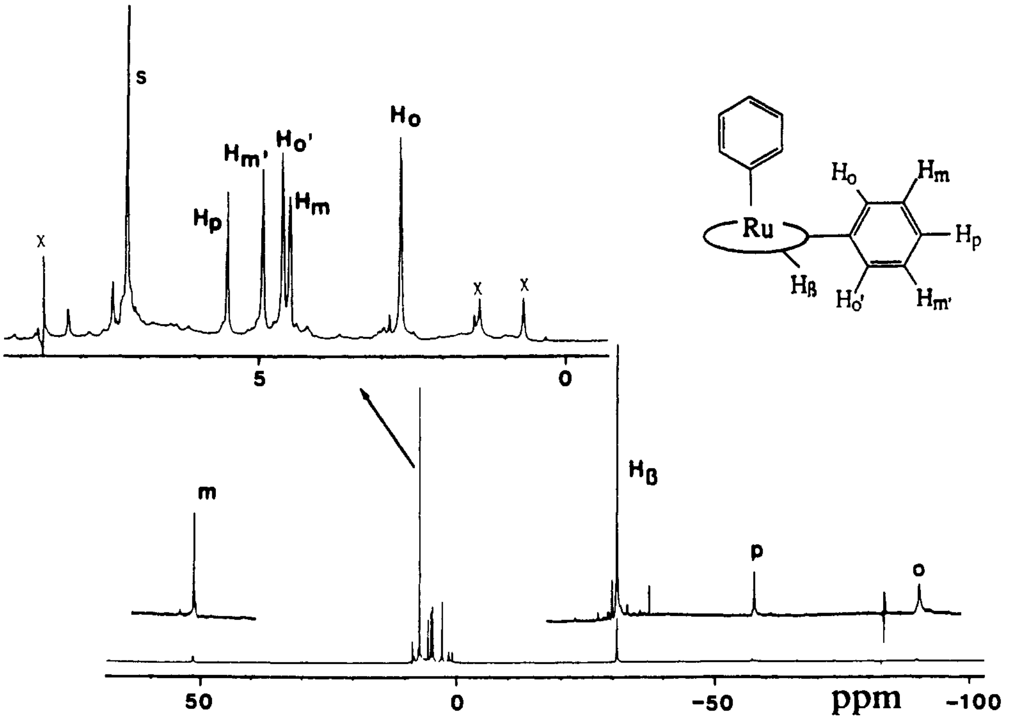

Figure 3. 400-MHz ^1H NMR spectrum of Ru(TPP)Ph in C_6D_6 at room temperature under anaerobic conditions. S = C_6H_6 residue; X = impurities. The letters o, m, and p refer to the ortho, meta, and para protons, respectively, of the axial phenyl ligand.

because of slow rotation of the phenyl groups.[44] The two doublets are readily assigned to H_o and $H_{o'}$, while decoupling of the δ 5.53 triplet results only in collapse of the other two triplets at δ 4.47 and 4.94 into doublets; this shows the latter two triplets correspond to H_m and $H_{m'}$ and the former corresponds to H_p. In addition, irradiation of the δ 2.65 doublet causes only collapse of the δ 4.47 triplet to a doublet, allowing for the associated assignments of H_o with H_m and of $H_{o'}$ with $H_{m'}$, although which set lies on the axial phenyl side (see Figure 3) is uncertain, as in the analogous Fe(TPP)Ph complex.[45]

The possibility of a dimeric, metal–metal bonded formulation $[Ru(TPP)Ph]_2$[18,46] is ruled out by (1) analogy to Ru(OEP)Ph (characterized crystallographically),[11] (2) the distinctive ^1H NMR spectrum, and (3) lack of formation of mixed species during a crossover experiment involving thermolysis of an equimolar mixture of $Ru(TPP)Ph_2$ and $Ru(OEP)Ph_2$.

The thermolysis of **5** to give **6** is a quantitative and clean reaction and can be monitored readily by UV/vis spectroscopy in the same manner reported for $Ru(OEP)Ph_2$;[11] the spectral changes with time during the conversion of **5** (λ_{max} 418 nm, log ϵ 5.02) to **6** (λ_{max} 411 nm, log ϵ 5.08) show three isosbestic points (cf. Figure 2 in ref 11) and can be analyzed by a standard procedure to yield a first-order rate constant k_1 that under appropriate conditions[11] refers to cleavage of the metal–carbon bond.[11,21b,47]

$$\mathrm{Ru(TPP)Ph_2} \xrightarrow{k_1} \mathrm{Ru(TPP)Ph} + \mathrm{Ph^{\bullet}} \tag{3}$$

In benzene solution, the phenyl radical product is seen as biphenyl; in toluene solution, the radical is consumed via pathways involving H abstraction from the solvent.[47,48] Over the limited temperature range 85–100 °C, the k_1 values in toluene increase from 2.59×10^{-5} to $18.9 \times 10^{-5}\ s^{-1}$ and yield an excellent Arrhenius plot from which $\Delta H_1^{\ddagger} = 34.2 \pm 0.6$ kcal/mol, a value 2.6 kcal higher then for the corresponding $Ru(OEP)Ph_2$ system.[11] The data conform to the trend of stronger axial ligand binding at a metalloporphyrin with decreasing porphyrin ligand basicity.[49] Further details on the estimation of the Ru–C bond energies (usually done by invoking a value of ~2 kcal/mol for the diffusion-controlled back-reaction of eq 3[9,11]) will be discussed in a later paper dealing with thermolysis of a series of $Ru(OEP)(aryl)_2$ complexes.[21b,47]

Solutions of **5** and **6** are stable under ambient, aerobic conditions in the dark. However, in the presence of laboratory light, the reddish benzene and toluene solutions of **6** (but not **5**) slowly become dark green on exposure to air or dry O_2, and the isolated product is characterized as the diamagnetic μ-oxo dinuclear species **7**.

$$\underset{\mathbf{6}}{4\mathrm{Ru(TPP)Ph}} + \mathrm{O_2} \xrightarrow{h\nu} \underset{\mathbf{7}}{2[\mathrm{Ru(TPP)Ph}]_2\mathrm{O}} \tag{4}$$

The ^1H NMR spectrum reveals data typical for a diamagnetic TPP system with an axial Ph ligand (cf. data for **5** discussed above). The singlet observed for the pyrrole β-H nucleus reveals C_4 symmetry, while the nonequivalent ortho and meta protons of the TPP phenyl group demonstrate lack of symmetry in the porphyrin plane. The axial ligand phenyl resonances appear as two triplets and a doublet with a 1:2:2 ratio, and the integrations correspond to one phenyl per TPP; the greater upfield shifts of these axial phenyl protons compared to those of **5** (by 2.73, 1.31, and 1.09 ppm for the ortho, meta, and para protons, respectively) perhaps result from the presence of ring currents from two porphyrin rings (versus one).

Complex **7** represents a further example within the class of well-substantiated species of the type $[Ru(por)X]_2O$, where por = TPP or OEP and X = halide, OH, OR (R = alkyl, aryl), HSO_4, or $OC(O)CF_3$.[18a,39,50] The elemental analysis for **7** is reasonable considering that trace impurities were observable in the ^1H NMR spectrum; the EI mass spectrum shows peaks assignable to $[Ru(TPP)O]^+$ and $[Ru(TPP)Ph]^+$, while a FAB spectrum reveals a peak at m/z 1597 assignable to $[\mathbf{7} - H]^+$. Some $[Ru(OEP)R]_2O$ complexes (R = aryl) have been studied more extensively and characterized more definitively.[21b,47] Cleavage of the O–O bond in O_2 by ruthenium porphyrins to give μ-oxo or terminal oxo

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species is well documented.[18a,27,39,51,52] Sometimes, trace H_2O is needed for formation of the μ-oxo species,[18a,39,51] but this is not so for reaction 4; eqs 5 and 6 represent a plausible mechanism,

$$Ru^{III} + O_2 \rightarrow RuO_2 \xrightarrow{Ru^{III}} Ru^{IV}\text{–O–O–}Ru^{IV} \rightarrow 2Ru^{V}O \quad (5)$$

$$Ru^{V}O + Ru^{III} \rightarrow Ru^{IV}\text{–O–}Ru^{IV} \quad (6)$$

$$(Ru = \mathrm{Ru(TPP)Ph})$$

which also rationalizes the nonreactivity of the coordinatively saturated complex **5** toward O_2. Analogous steps have been demonstrated for the conversion of Fe(II) porphyrins to dinuclear Fe(III) μ-oxo species[53] and may well prevail for corresponding Ru(II) porphyrins.[54] Literature precedent for the steps of eqs 5 and 6 exists for the proposed Ru/oxygen-containing species within macrocyclic (but non-porphyrin) systems involving O_2.[55]

To our knowledge, the retention of the metal–carbon bond during a light-induced reaction of O_2 with an organometallic porphyrin complex, as in eq 4, is unique. In $\mathrm{Fe(TPP)(CH_2R)}$ systems (R = H, alkyl, Ph), photolysis cleaves the Fe–C bond and aldehyde or ketones together with the Fe(III)–μ-oxo species result from decomposition of an $\mathrm{FeO_2CH_2R}$ intermediate;[56] in the related Fe(OEP)Ph system, the Ph radical appears as biphenyl.[57] In cobalt[58] and main-group porphyrin complexes,[59] the products formed are metal–OOR species. More generally, the photochemical and thermochemical reactions of alkyl- and aryl-metalloporphyrin complexes have been to date dominated by initial cleavage of the metal–carbon bond.[60]

In the present Ru system, a mechanism initiated by cleavage of the Ru–C bond is difficult to imagine, and the nature of the photochemical step remains to be established.

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Supplementary Material Available: Tables SI and SII, giving additional crystallographic details and anisotropic thermal parameters (3 pages); Table SIII, listing structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Synthesis of Complexes of Rhodium(I) and Iridium(I) with 3,5-Pyrazoledicarboxylic Acid and Their Mixed-Valence Oxidation Products

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The ability of the trianion of 3,5-pyrazoledicarboxylic acid (H_3Dcbp) to form dinuclear complexes has been utilized in the preparation of a family of anionic complexes of rhodium(I) and iridium(I) using 1,5-cyclooctadiene, CO, and PPh_3 as ancillary ligands. The complex $\mathrm{(NBu_4)[Rh_2(CO)_4Dcbp]}$ crystallizes in the $P\bar{1}$ space group with a = 13.043 (5) Å, b = 13.543 (3) Å, c = 10.702 (3) Å, α = 109.91 (2)°, β = 112.06 (2)°, γ = 95.56 (2)°, V = 1591.5 (8), and Z = 2. The complex anion is nearly planar and has a short intermolecular distance between the rhodium atoms. Stacking interactions in some of the rhodium and iridium anionic carbonyl complexes in the solid state can be inferred from the dramatic change of color with changes in the countercation. The electrochemical oxidation of $\mathrm{(NR_4)[Ir_2(CO)_4Dcbp]}$ (R = Bu, Pr) produced dark materials growing on the anode surface of the electrode. The solid analyzed as $\mathrm{(NR_4)_{0.5}[Ir_2(CO)_4Dcbp]}$. Pressed-pellet conductivities of these materials are in the range $10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which are 1000 times higher than the unoxidized precursor. X-ray photoelectron spectroscopy corroborates the stoichiometry of these compounds and indicates that both iridium atoms in the dinuclear unit are involved in the formation of stacks with delocalized mixed valence.

Introduction

Synthesis and characterization of solids with extended intermolecular interactions is of great interest due to their unique physical and chemical properties. Study of electron transfer in the solid state is of particular importance because it leads to understanding of a variety of fundamental processes. The interactions present in mixed-valence or conducting-chain materials illustrate the delicate balance between local and extended interactions. However, the number of distinct anisotropically conducting materials remains quite limited. Among the metal chain systems are the well-known cyano and oxalato complexes of platinum and the chlorocarbonyl complexes of iridium.[1] We have

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