Five-Co-ordinate Aryl- and Alkyl-Ruthenium(III) Porphyrin Complexes, and Ruthenium–Carbon Bond Strengths

Mingzhe Ke, Steven J. Rettig, Brian R. James,* and David Dolphin*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

The ruthenium(III) complex Ru(OEP)Ph† has been isolated and characterized crystallographically; its formation by the thermal decomposition of Ru(OEP)Ph$_2$ allows an estimation of a Ru–C(sp^2) bond strength.

We reported recently on the synthesis and characterization of the Ru^{IV} complexes Ru(OEP)R$_2$† (R = alkyl or aryl),[1] and now wish to document the novel chemistry outlined in equations (1) and (2). Complexes (**1**) and (**2**) have been fully characterized, including an *X*-ray crystallographic analysis of

$$\mathrm{Ru(OEP)Ph_2} \xrightarrow{\text{heat}} \underset{(\mathbf{1})}{\mathrm{Ru(OEP)Ph}} + (1/2)\mathrm{Ph_2} \qquad (1)$$

$$2\mathrm{Ru(OEP)Me_2} \xrightarrow{\text{heat}} \underset{(\mathbf{2})}{2\mathrm{Ru(OEP)Me}} + \mathrm{CH_4} + (1/2)\mathrm{CH_2{=}CH_2} \qquad (2)$$

the phenyl complex.‡ This is the first reported metalloporphyrin structure involving an organoruthenium fragment, the data complementing those published for the Fe(TPP)Ph complex.[3a] Information on the structure and reactivity (clearly radical in nature) of organoruthenium porphyrin species should aid the understanding of the role of organoiron intermediates in some haem chemistry[3,4] and is of interest for comparison with vitamin B$_{12}$ systems, particularly concerning the strengths of the metal–carbon bonds, their dissociation energies being readily gleaned from reactions such as (1) and (2) (*vide supra*).[5]

The five-co-ordinate, low-spin complexes Ru(OEP)R (R = Ph, *m*-MeC$_6$H$_4$, *p*-MeC$_5$H$_4$, and Me) are formed *via* anaerobic thermolysis at *ca.* 100 °C of the Ru(OEP)R$_2$ complexes in toluene or benzene solution; yields are quantitative at spectroscopic (n.m.r. and u.v.–vis) and preparative levels (~50 mg in 10 ml solvent). Complex (**1**) has been characterized crystallographically,§ and its structure is shown in Figure 1.

The structure is essentially square pyramidal, with the metal displaced 0.122 Å from the N$_4$ plane towards the phenyl group. The average Ru–N distance of 2.030 Å, and the angles and distances for the porphinato core, are similar to those found for the low-spin species RuBr(OEP)PPh$_3$[6] and Ru(TPP)(OEt)EtOH.[7] The low-spin state (S = 1/2) of (**1**) is compatible with that found in Fe(porph)Ph (porph = OEP, TPP), which results from the high field strength of the σ-aryl ligand.[3] The Ru–C bond distance of 2.005 Å, which is, as expected, somewhat longer than the Fe–C distance (1.955 Å) found in Fe(TPP)Ph,[3a] is at the lower end of the Ru–C(sp^2) σ-bonded distances reported to date (1.997—2.190 Å),[8] including bonding to phenyl[8d,e] and naphthyl[8f] moieties; the phenyl ring within (**1**) has normal geometry, and the relative shortness of the Ru–C bond must reflect in part the absence of a *trans*-co-ordinated ligand.

The ^{1}H n.m.r. spectra of all the complexes (Table 1) are consistent with the presence of paramagnetic Ru^{III} species,[5,6] the chemical shifts of the porphyrin ring and axial aryl protons showing large paramagnetic shifts from their positions in related, diamagnetic Ru^{II}[9] and Ru^{IV}[1] complexes; particularly noticeable is the large chemical shift difference between the methylene protons that are anisochronous because of the lack

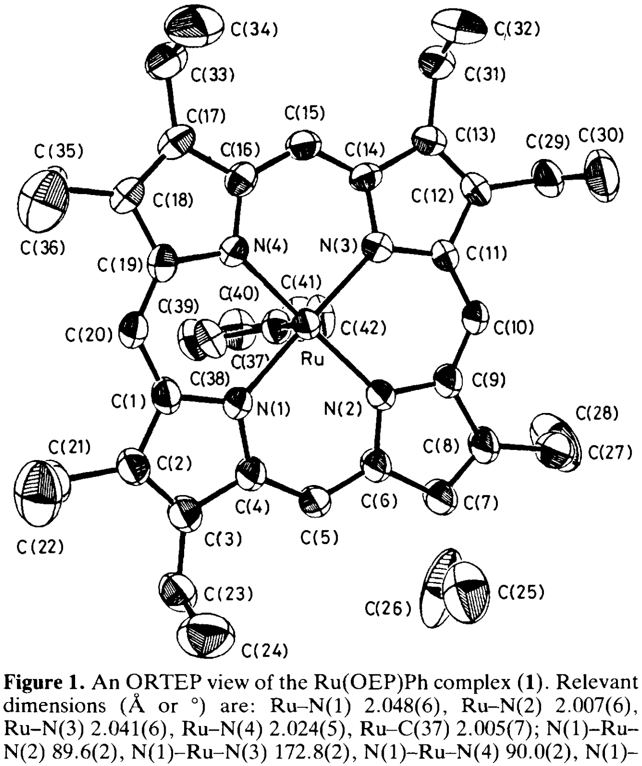

Figure 1. An ORTEP view of the Ru(OEP)Ph complex (**1**). Relevant dimensions (Å or °) are: Ru–N(1) 2.048(6), Ru–N(2) 2.007(6), Ru–N(3) 2.041(6), Ru–N(4) 2.024(5), Ru–C(37) 2.005(7); N(1)–Ru–N(2) 89.6(2), N(1)–Ru–N(3) 172.8(2), N(1)–Ru–N(4) 90.0(2), N(1)–Ru–C(37) 93.1(3), N(2)–Ru–N(3) 90.1(2), N(2)–Ru–N(4) 173.4(2), N(2)–Ru–C(37) 92.0(3), N(3)–Ru–N(4) 89.5(2), N(3)–Ru–C(37) 94.1(3), N(4)–Ru–C(37) 94.7(3), N(1)–C(37)–C(38) 36.4(7).

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† Abbreviations used: OEP, TPP = dianions of 2,3,7,8,12,13,17,18-octaethylporphyrin and 5,10,15,20-tetraphenylporphyrin, respectively; tmpo = 2,2,6,6-tetramethylpiperidine-1-oxyl; py = pyridine.

‡ Complexes (**1**) and (**2**) have been characterized by elemental analyses, mass and n.m.r. (Table 1) spectroscopy, and solution magnetic moments[2] (μ_{eff} = 1.9 ± 0.1 μ_B).

§ *Crystal data* for (**1**): Ru(OEP)Ph·(1/2)C$_6$H$_6$, monoclinic, space group $P2_1/n$, a = 14.679(1), b = 16.528(1), c = 15.841(1) Å, β = 94.121(6)°, U = 3833.4(4) Å^3, Z = 4, D_c = 1.299 g cm^{-3}. Intensity data were collected at 25 °C on an Enraf-Nonius CAD4-F diffractometer with nickel-filtered Cu-K_α radiation ($2\theta \leqslant 150°$), μ(Cu-K_α) = 36.3 cm^{-1}, F(000) = 1576. The structure was solved using Patterson and Fourier techniques and was refined by full-matrix least-squares procedures to R = 0.057 and R_w = 0.062 for 4291 absorption-corrected data with $I \geqslant 3\sigma(I)$. Crystal dimensions were 0.25 × 0.35 × 0.45 mm. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were fixed in idealized positions. The ethyl group attached to C(7) is disordered, but no satisfactory disordered model could be refined. The best results were obtained when the regions of maximum electron density were refined as full-occupancy carbon atoms [C(25) and C(26)]. These positions are best interpreted as the midpoints of the C$_\alpha$–C$_\beta$ bonds for the two orientations of the disordered ethyl group. The difficulty in resolution of the disorder may be ascribed to the large component of thermal motion normal to the porphyrin plane in that portion of the molecule.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. ^{1}H N.m.r. chemical shifts (δ) for Ru(porph)R derivatives (R = aryl, Me).[a]

		Porphyrin ring		R		
Complex	H_{meso}	CH_2	CH_3	H_o	H_m	H_p
Ru(OEP)Ph, (**1**)	1.14	14.13, 5.81	−1.02	−83.05	48.82	−48.84
Ru(OEP)(m-MeC$_6$H$_4$)	1.24	13.85, 5.92	−1.02	−84.04 −86.56	48.24 −14.42[b]	−51.19
Ru(OEP)(p-MeC$_6$H$_4$)	1.82	13.94, 5.77	−0.93	−95.88	49.37	108.96[b]
Ru(OEP)Me, (**2**)	−0.24	11.62, 5.70	−1.78		[c]	
Ru(OEP)Ph(py)[d]	−3.04	10.50, 6.80	−1.82	−60.10	49.16	−33.92
Ru(OEP)Ph(PBu$^n{}_3$)[e]	−3.88	12.70, 8.53	−0.77	−31.82	44.34	−23.10
Ru(TPP)Ph[f]		[g]		−89.53	51.65	−57.47

[a] Measured at 400 or 300 MHz in C_6D_6 at ambient conditions *in vacuo*; relative integrations for protons are consistent with the assignments; signals are all broadened singlets, and those downfield are written as positive. [b] Me resonance. [c] The methyl ligand signal is not observed because of extreme line broadening.[5] [d] Py resonances observed in CD_2Cl_2 at δ 18.3 (br.). [e] Bu^n signals seen at δ 20.59(6H), 9.55(6H), 4.20(6H), and 2.40(9H). [f] This TPP complex is formed by thermal decomposition of Ru(TPP)Ph$_2$ [*cf.* equation (1)], which itself is synthesized from the dihalides Ru(TPP)Br$_2$, *cf.* ref. 1. [g] Porphyrin ring signals: pyrrole-H, δ −30.94; H_o, doublets at δ 2.65, 4.60; H_m, triplets at δ 4.47, 4.94; H_p, triplet at δ 5.53.

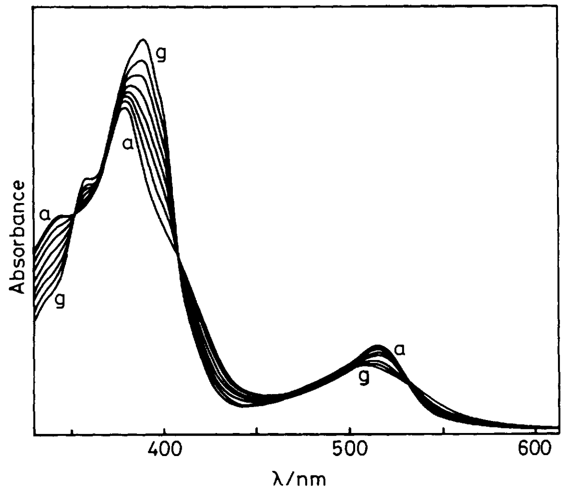

Figure 2. U.v.–visible absorption spectral changes (measured at 25 °C) for the thermolysis of Ru(OEP)Ph$_2$ in toluene at 97 °C, equation (1), carried out in a tonometer sealed under vacuum; curves a—g measured at times 0, 8, 21, 35, 52, 71, 93, and 500 × 10^2 s, respectively.

of a porphyrin plane of symmetry. The ^{1}H n.m.r. behaviour resembles closely that of the low-spin Fe(porph)(aryl) complexes.[3b,c] Further, the temperature dependence of the isotropic shifts for the porphyrin protons of (**1**) and (**2**) follows Curie behaviour with strictly linear dependences of shift *vs.* T^{-1} from 200—350 K, showing that a single spin state exists over this temperature range.

Reactions (1) and (2) are remarkably clean. For example, diphenyl is formed in close to quantitative yield, and monitoring the reaction by u.v.–visible spectroscopy shows excellent isosbestic behaviour (Figure 2). The spectral changes shown correspond to a standard first-order process from which rate constants (k_1) are readily evaluated; the reaction is unaffected by light, and the rates are independent of an added free-radical scavenger such as tmpo,[10] showing that k_1 refers to the rate-determining step, homolytic cleavage of the Ru–C bond; *i.e.*, $k_2 \gg k_{-1}$ in equation (3). Over the limited temperature range of 85—100 °C, the respective k_1 values increase from 4.85 to 28.6 × 10^{-5} s^{-1} and yield an excellent Arrhenius plot from which $\Delta H^{\ddagger}_1 = 31.6 \pm 0.5$ kcal/mol (1 cal = 4.184 J), which is an upper limit of the metal–carbon bond energy. If the k_{-1} radical combination step is close to being diffusion-controlled, as demonstrated for reaction of Co^{II} with alkyl radicals, where the corresponding $\Delta H^{\ddagger}{}_{-1}$ value is *ca.* 2 kcal/mol,[11] the Ru–C(sp^2) bond dissociation energy can be given as 29.6 ± 0.5 kcal/mol. This value is about 8 kcal/mol higher than that estimated[5] for dissociation of the ethyl radical from Ru(OEP)Et$_2$; stronger metal–carbon bonding for aryls *vs.* alkyls is well documented for the group 4 transition metals[12] but, to our knowledge, no such comparable data are available for other transition metals (it is noteworthy that homolytic cleavage of the C–H bond within benzene requires some 13 kcal/mol more than for that within ethane[13]).

$$\text{Ph–Ru(OEP)–Ph} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PhRu(OEP)} + \text{Ph}\cdot \ (2\text{Ph}\cdot \xrightarrow{k_2} \text{Ph}_2) \qquad (3)$$

The decomposition of (**2**) follows the stoicheiometry shown in equation (2),¶ and in [$^2H_6$]benzene no deuterium is incorporated into any of the products. The mechanism outlined in equations (4)—(6), which invokes well-precedented α-hydrogen abstraction to give an undetected methylidene intermediate,[14] accounts nicely for the stoicheiometry.|| As well as the interesting organometallic chemistry observed for the Ru^{IV} dialkyl species (see also refs. 5 and 14), kinetic studies on reaction (1) for a series of diaryl species should provide a useful addition to the very limited data base for 'solution' bond energies of organometallics.[5,12,15] Of note in this regard, complex (**1**) readily binds a second axial ligand

$$\text{MeRuMe} \rightarrow \text{RuMe} + \text{Me}\cdot \qquad (4)$$

$$\text{MeRuMe} + \text{Me}\cdot \rightarrow \text{'MeRu=CH}_2\text{'} + \text{CH}_4 \qquad (5)$$

$$2\text{'MeRu=CH}_2\text{'} \rightarrow 2\text{RuMe} + \text{CH}_2\text{=CH}_2 \qquad (6)$$

¶ The CH_4 and C_2H_4 were detected by g.c. (Porapak column, He carrier, 25 °C) in a ratio of *ca.* 1.8 : 1; the rate of decomposition was found to be dependent on the concentration of tmpo which also appears to react with Ru(OEP)Me.

|| The reported decomposition of Ru(OEP)Et$_2$ is more complex because of competing α- and β-hydrogen abstraction processes in pathways corresponding to equation (5).[5]

(L); *e.g.* pyridines and phosphines (see Table 1). The six-co-ordinate derivatives are readily isolated and, on dissolution in toluene, dissociative equilibria to complex (**1**) and free L are established. Aryl derivatives of (tetraphenylporphinato)ruthenium can also be readily synthesized, and their chemistry is akin to that of the OEP systems (Table 1, footnote f).

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