

Dihalogeno-, Diphenyl-, and Dialkyl-ruthenium(IV) Porphyrin Complexes

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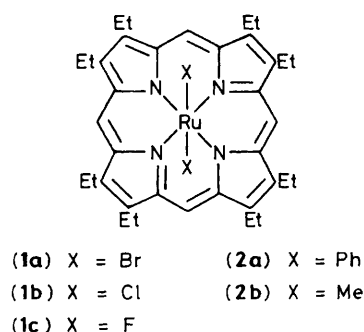
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Halogen oxidation of $[\text{Ru}(\text{OEP})]_2$ (OEP = dianion of octaethylporphyrin) yields the paramagnetic dihalogenoruthenium(IV) complexes $\text{Ru}(\text{OEP})\text{X}_2$, which on treatment with the appropriate aryl- or alkyl-lithium reagent readily give the corresponding diamagnetic organometallic derivatives $\text{Ru}(\text{OEP})\text{R}_2$.

Organometallic chemistry at metalloporphyrin centres is of intense current interest, and plays key roles, for example, in cytochrome P450 and vitamin B₁₂ systems.^{1,2} Further, recent communications on the formation of ruthenium porphyrin organometallics *via* reaction of electrophiles with porphyrinato-ruthenium(0) dianions,³ and on a (dioxo)porphyrinato-ruthenium(VI)-catalysed aerobic epoxidation of alkenes,⁴ prompt us to report a method for the synthesis of dihalogeno(octaethylporphyrinato)ruthenium(IV) com-

plexes; these should be important precursors for Ru^{IV} porphyrin chemistry generally, and this is exemplified by simple routes to diphenyl and dialkyl derivatives.

Dichloromethane (20 ml), saturated with anhydrous HX (Matheson, 99.8%), was vacuum transferred to the $[\text{Ru}(\text{OEP})]_2$ dimer⁵ (0.1 mmol); the deep red solution formed at ambient temperatures is air-stable, and yields $\text{Ru}(\text{OEP})\text{X}_2$ (OEP = dianion of octaethylporphyrin) (**1a**), X = Br, (**1b**), X = Cl, and (**1c**), X = F, on addition of hexane. Recrystalliza-



tion from CHCl_3 -hexane yields the pure complexes in 80% yield; the elemental analyses, including halide (except for F^-), are correct, and the spectroscopic data for the e.s.r.-silent, paramagnetic complexes (the solution magnetic moments, $\mu_{\text{eff}} = 2.5\text{--}2.7 \mu_{\text{B}}$, correspond to two unpaired spins), which are essentially non-conducting in MeCN, are entirely consistent with a monomeric *trans*- $\text{Ru}(\text{OEP})\text{X}_2$ formulation {for (1a): ^1H n.m.r.† δ (20 °C, CDCl_3), all broad singlets, 60.1 (16H, CH_2), 7.10 (24H, CH_3), and 3.50 (4H, *meso*-H); i.r. $\nu(\text{RuBr})$ 174 cm^{-1} ; u.v.-vis. (CHCl_3) λ_{max} (log ϵ), 360 (4.71), 398 (4.91), 505 (4.22), and 535 (4.12) nm; mass spectrum (electron impact) m/z [$M - \text{Br}$] $^+$ 713, [$M - 2\text{Br}$] $^+$ 634, and $\text{Br}^+ 80$ }. The proton resonances are paramagnetically shifted compared to their positions in diamagnetic species,^{5,7} the ethyl protons downfield and the *meso* protons upfield; that the methylene protons are non-anisochronous reveals mirror symmetry in the porphyrin plane.⁵ The n.m.r. and u.v.-visible data for (1b) (νRuCl , 284 cm^{-1}) and (1c) are very similar to those for (1a), except that the *meso* protons are seen at δ 8.89 and 9.63, respectively. To our knowledge, complexes (1a)–(1c) are the first reported monomeric, paramagnetic Ru^{IV} porphyrin complexes;⁸ a few such Fe^{IV} species have been reported recently.⁹

The mechanism of formation of the $\text{Ru}(\text{OEP})\text{X}_2$ complexes has not been established, but traces of halogen in the HX reagents are considered to be responsible for the oxidation; the preparative procedure can be reversed by heating {for example, after 1 h at 200 °C and 10^{-5} Torr, (1a) regenerates $[\text{Ru}(\text{OEP})]_2$ quantitatively}. The halogens themselves can be used for the oxidation, but more side-products are formed and the HX treatment is much preferred; the syntheses are reproducible using either new or old samples from Matheson. Radical processes may play a role as in some related Rh porphyrin chemistry.¹⁰ We have been unable to detect H_2 during formation of the dibromo complex, which tends to rule out reaction *via* oxidative addition of, and subsequent attack by, HX. Dioxygen, especially in the presence of protons, can oxidise ruthenium(II) porphyrins,¹¹ but the preparative conditions are anaerobic and traces of O_2 are unlikely to be the oxidant.

Addition of RLi (5 equiv.) in ether ($\text{R} = \text{Ph}$ or Me) to (1a) (0.15 mmol) dissolved in C_6H_6 (200 ml) readily gives the $\text{Ru}(\text{OEP})\text{R}_2$ derivatives (2a), $\text{R} = \text{Ph}$ and (2b), $\text{R} = \text{Me}$. The reaction mixture is washed with H_2O (3×100 ml) and the organic phase then chromatographed (alumina I, C_6H_6). The resulting products, recrystallized from CH_2Cl_2 -MeOH and vacuum-dried (35% yield), are analytically pure, diamagnetic

and are characterized spectroscopically (^1H n.m.r. δ (20 °C, CDCl_3), (2a): 9.68 (s, 4H, *meso*-H), 5.32 (t, 2H, H_p), 4.86 (m, 4H, H_m), 3.80 (q, 16H, CH_2), 1.77 (t, 24H, CH_3), and 0.61 (d, 4H, H_o); for (2b), the data are essentially the same as those recently reported for $[\text{H}_8]$ tetrahydrofuran solutions of the complex;³ u.v.-vis. (CH_2Cl_2) λ_{max} (log ϵ), (2a): 377 (4.82) and 516 (4.27) nm; (2b): 334 (4.80), 377 (5.04), and 5.43 (4.12) nm; mass spectrum m/z (electron impact), (2a): [$M - \text{H}$] $^+$ 787, [$M - \text{Ph}$] $^+$ 711, [$M - 2\text{Ph}$] $^+$ 634, and C_6H_6^+ 78; (2b): [$M - \text{H}$] $^+$ 663, [$M - \text{CH}_3$] $^+$ 649, [$M - 2\text{CH}_3$] $^+$ 634.} The $\text{Ru}(\text{OEP})\text{Et}_2$ species has been prepared similarly in solution; the ^1H n.m.r. signals of the Ru-bonded Et groups (CH_2 , δ -2.74, q; CH_3 , -4.54, t) correspond closely to those found for the corresponding tetra-*p*-tolylporphyrinato analogue.³

The porphyrin ring ^1H n.m.r. shift for the dialkyls and diphenyl porphyrin are typical for diamagnetic species containing OEP,^{5,7} and the upfield phenyl resonances correspond to those found in other diamagnetic diphenyl porphyrin complexes.¹²

Complex (2b) can be made also by treating $\text{Ru}(\text{OEP})\text{-(P}^n\text{Bu)}_3\text{Br}$ ¹³ with MeLi, but its isolation requires separation from the $\text{Ru}(\text{OEP})(\text{P}^n\text{Bu})_2$ co-product.¹³ The Ru-C bonds within (2a) and (2b) are readily cleaved by acids; for example, reaction with HBr in CH_2Cl_2 yields (1a).

The $S = 1$ state for (1a)–(1c) is explained by d^4 occupancy of a closely spaced t_{2g} set (with either d_{xy} or $d_{xz,yz}$ being lowest in energy¹⁴), while the $S = 0$ state for (2a) and (2b) requires the electrons to be accommodated in a lower $d_{xz,yz}$ set. Presumably, the π -donor properties of the halides tend to destabilize the $d_{xz,yz}$ set within the $\text{Ru}(\text{OEP})\text{X}_2$ species.

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† Signals downfield are written as positive throughout this communication; the paramagnetic convention is not used.