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Synthesis of Ruthenium(III) and Osmium(III) Porphyrin Mono-alkyl and -aryl Complexes and of a Novel Six-coordinate Asymmetrically Substituted Ruthenium(IV) Porphyrin Complex, [Ru(oep)(Ph)(Me)]†

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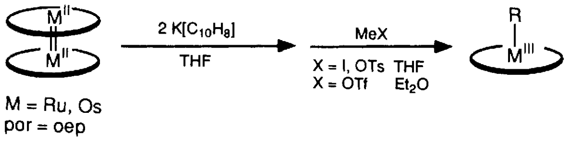
M^{III} porphyrin monoalkyl complexes, [M(oep)(Me)] (M = Ru, Os), are produced by methylation of the monomer monoanion, $[M(oep)]^-$, or by addition of MeMgBr to the $[M(oep)]_2^{2+}$ dimer dication; the Ru^{III} monophenyl complex, [Ru(oep(Ph)], can be reduced by one electron and treated with MeI to give the six-coordinate asymmetrically substituted Ru^{IV} porphyrin complex, [Ru(oep)(Ph)(Me)].

The Ru^{II} and Os^{II} porphyrin dimers $[M(por)]_2$ (M = Ru, Os; por = oep,† ttp†) are extremely useful for the study of multiple metal–metal bonds and exhibit a rich and varied chemistry.[1] The Ru^{II} and Os^{II} porphyrin dimers are cleaved upon reduction by four electrons and the resulting nucleophilic metalloporphyrin dianions react with electrophiles to produce both organometallic and inorganic Ru and Os porphyrin complexes.[2a] For example, $[M(por)]^{2-}$ (M = Ru, Os; por = oep, ttp) react with alkyl halides,[2] tosylates,[2a] and triflates[2a] to generate six-coordinate Ru^{IV} and Os^{IV} porphyrin dialkyl complexes. Alternatively, Ru^{IV} dialkyl complexes can be prepared by treatment of Ru^{IV} porphyrin dihalides, $[Ru(oep)(X)_2]$, with alkyl or aryl lithium reagents.[3] The five-coordinate Ru^{III} porphyrin mono-alkyl and -aryl complexes can be formed by the homolytic decomposition of six-coordinate Ru^{IV} porphyrin di-alkyl or -aryl complexes.[2c,4] We report now the preparation of five-coordinate mono-alkyl and -aryl Ru^{III} and Os^{III} porphyrin complexes by alternative routes and the synthesis of a six-coordinate Ru^{IV} porphyrin complex having two different organic axial ligands.

The metalloporphyrin dimer $[Ru(oep)]_2$ was dissolved in freshly purified THF and 2 equiv. of potassium naphthalenide[5] in THF were slowly added with rapid stirring; the solution colour changes from green-brown to dark-red. After stirring for 5–10 min, the putative monomeric monoanion $[Ru(oep)]^-$ was methylated with methyl iodide, methyl tosylate or methyl triflate in THF or Et_2O to yield a dark orange-red solution of [Ru(oep)(Me)] (Scheme 1). The spectral characteristics of this complex‡ agree with those observed for this complex synthesized by an independent method.[4] Similarly, $[Os(oep)]_2$ treated by 2 equiv. of $K[C_{10}H_8]$ in THF and then MeX (X = I, OTs, OTf) in THF or Et_2O afforded $[Os(oep)(CH_3)]$.‡

The five-coordinate Ru^{III} and Os^{III} porphyrin mono-alkyl and -aryl complexes can be generated by an alternative route. Treatment of the dimer dications, $[M(oep)]_2(BF_4)_2$, obtained by oxidation of $[M(oep)]_2$ by $AgBF_4$,[6] with a stoichiometric amount of a Grignard reagent or organozinc compound in Et_2O yields (after flash silica chromatography in an inert atmosphere dry box under subdued light) the mono-alkyl and -aryl M^{III} porphryin complexes, [M(oep)(R)] (M = Ru, Os; R = Me, Et, Ph, p-MeC_6H_4; measured yields range from 46 to 75%) [eqn. (1)]. Any metalloporphyrin di-alkyl or -aryl side products can be converted to the five-coordinate monoalkyl or monoaryl complexes by thermolysis.[4] Addition of alkyl and aryl lithium reagents to the dimer dications largely results in electron transfer reactions.

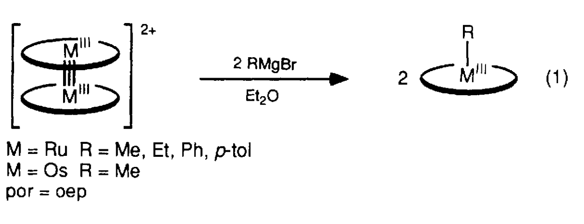


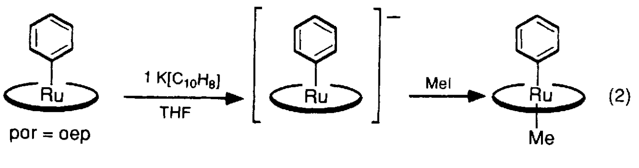
Scheme 1

Since the monomer dianion, $[Ru(oep)]^{2-}$, and the monomer monoanion, $[Ru(oep)]^-$, react with alkylating agents to give the di- and mono-alkyl complexes respectively, a reduced mono-alkyl or -aryl complex, $[Ru(oep)(R)]^-$, is also expected to exhibit reactivity with carbon electrophiles. If the one-electron reduction product of $[Ru^{III}(oep)(R)]$ species has $[Ru^{II}(oep)(R)]$ character, reaction with an alkylating agent could yield a six-coordinate organometallic Ru^{IV} porphyrin complex. This reaction would constitute a synthetic method for the preparation of novel asymmetric $[Ru^{IV}(por)(R)(R')]$ complexes in which two different axial ligands are present.

When potassium naphthalenide (1 equiv.) is slowly added to [Ru(oep)(Ph)] in THF under an inert atmosphere, the anionic $[Ru(oep)(Ph)]^-$ complex is generated.[7] Subsequent addition of MeI forms the disubstituted organometallic porphyrin complex, [Ru(oep)(Ph)(Me)] [eqn. (2)].‡

The diamagnetic unsymmetric $[Ru^{IV}(oep)(Ph)(Me)]$ complex has a diagnostic ^1H NMR spectrum. The methylene protons of the oep ligand are diastereotopic and appear as a multiplet indicative of axial asymmetry. The proton resonances of the axial phenyl and methyl ligands exhibit characteristic upfield shifts resulting from the porphyrin ring effect, but are distinct from the resonances of the axial ligands of the $[Ru(oep)(Me)_2]$ and $[Ru(oep)(Ph)_2]$ complexes.[2a,3] The integrals of the NMR signals indicate one phenyl ligand and one methyl ligand in the complex. The [Ru(oep)(Ph)(Me)] complex is thermally labile and slowly decomposes to [Ru(oep)(Ph)] over several weeks when stored as a solid in an inert atmosphere box at room temp. This is in good agreement with the estimated metal–carbon bond dissociation energies of $[Ru(oep)(Ph)_2]$ 124 ± 2 kJ mol^{-1} [4] and $[Ru(oep)(Et)_2]$ 91 ± 6 kJ mol^{-1}.[2b] Homolytic decomposition of [Ru(oep)(Ph)(Me)] is expected to yield [Ru(oep)(Ph)] as is observed. Mass spectra data also indicate that the complex is fragile. The parent molecular ions have been observed in the mass spectra data (EI) of $[Ru(oep)(Me)_2]$,[3] $[Ru(ttp)(Me)_2]$,[2b] and $[Ru(oep)(Ph)_2]$.[3] In contrast, only the fragments resulting from the loss of an axial methyl or phenyl ligand were observed in the EI mass spectrum [Ru(oep)(Ph)(Me)].





However, the molecular ion of the parent complex, [Ru(oep)(Ph)(Me)] was successfully detected by FABMS.† Still, the largest molecular ions observed were those of the fragments $[Ru(oep)(Ph)]^+$ and $[Ru(oep)(Me)]^+$ resulting from the homolysis of the Ru–C_{methyl} and the Ru–C_{phenyl} bonds.

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Footnotes

† *Abbreviations used*: por = porphyrin dianion unspecified; oep = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion; ttp = 5, 10, 15, 20-tetra-*p*-tolylporphyrin dianion; THF = tetrahydrofuran; MeOTf = methyl triflate; MeOTs = methyl tosylate; FABMS = fast atom bombardment mass spectrometry; NDCI = negative desorption chemical ionization mass spectrometry.

‡ *Selected NMR data*: [Ru(oep)(Me)]: ^1H NMR (400 MHz, C_6D_6) δ H_{meso} −1.25 (br s, 4 H), CH_2 11.65 (br s, 8 H), 5.46 (br s, 8 H), Me −2.03 (s, 24 H), (Ru–Me not observed due to extreme line broadening); ^1H NMR ([$^2H_8$]THF) δ H_{meso} −3.11 (br s, 4 H), CH_2 8.59 (br s, 8 H) 5.54 (br s, 8 H), Me −2.34 (br s, 24 H), (Ru–Me not observed due to extreme line broadening); UV–VIS/nm (C_6H_6) 341 (sh), 360, 394 (Soret), 474 (sh) 503; MS(NDCI) m/z = 649, cluster, M^-; 634, cluster, M^-–Me.

[Os(oep)(Me)]: ^1H NMR (C_6D_6) δ H_{meso} 1.34 (br s, 4 H, obscured), CH_2 5.55 (br s, 8 H), 2.03 (br s, 8 H), Me −3.03 (br s, 24 H) (Os–Me not observed due to extreme line broadening); UV–VIS/nm (C_6H_6) 339, 357 (sh), 378 (Soret), 447, 478, 520 (sh); MS(NDCI) m/z = 739, cluster, M^-; 725, cluster, M^- + H–CH_3.

[Ru(oep)(Ph)(Me)]: ^1H NMR (C_6D_6) δ H_{meso} 9.90 (s, 4 H), CH_2 3.73 (m, 16 H), CH_3 1.77 (t, 7.6 Hz, 24 H), C_6H_5 H_p 5.04 (t, 6.6 Hz, 1 H), H_m 4.87 (t, 7.8 Hz, 2 H), H_o 1.24 (d, 8.6 Hz, 2 H), Me −2.74 (s, 3 H); FABMS (sulfolane matrix, positive ion mode) m/z = 726, cluster, M^+; 711, cluster, M^+ − Me; 649, cluster, M^+ − Ph; 634, cluster, M^+ − Me − Ph. New compounds have been characterized by NMR, UV–VIS and mass spectroscopies. The limited quantities of these metalloporphyrin complexes hindered their characterization by other methods.

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