Redox Pathways of $Ru(OEP)(Ph)_2$ and Ru(OEP)(Ph) (OEP = Octaethylporphyrin dianion)

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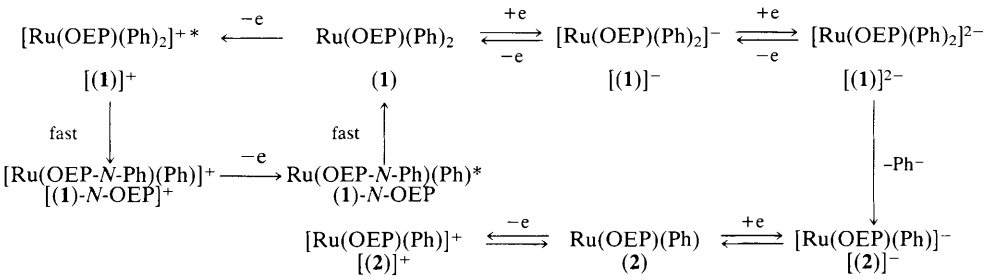
Electrochemical, chemical, and spectroscopic methods reveal the redox and coupled reaction pathways of the organometallic porphyrin complex $Ru(OEP)(Ph)_2$ (OEP = octaethylporphyrin dianion) (**1**) and the corresponding monophenyl complex (**2**), an intermediate in the redox reactions of (**1**).

The redox and reaction chemistry of organometallic porphyrin complexes is an intriguing area of inorganic and bioinorganic chemistry,[1] as exemplified by the work of Kadish[2—5] on the electrochemistry of iron,[3] rhodium,[4] iridium,[5] and related[2] organometallic porphyrin complexes. The synthetic routes to ruthenium porphyrin alkyl[6—8] and aryl[8—9] complexes developed by Collman[6—7] and Dolphin[8—9] provide new organometallic porphyrin chemistry to explore and to compare with that of other metalloporphyrin complexes, particularly to the iron complexes. We report herein the first study of redox and



(* Species not observed.)

Scheme 1. Redox and accompanying chemical reactions of (**1**) and (**2**).

associated reaction chemistry of ruthenium-aryl organometallic porphyrin complexes.

Complex (**1**) was prepared by reaction[8] of $Ru(OEP)Cl_2$ (OEP = octaethylporphyrin dianion) and PhLi/tetrahydrofuran (THF) in C_6H_6. Chromatography on Al_2O_3 with C_6H_6/hexanes eluent separated the desired product from a *ca.* 10% impurity of Ru(OEP)(Ph) (**2**) (*vide infra*). The cyclic voltammetric response of (**1**) in 0.2 M Bu_4NClO_4/THF at a Pt disc electrode is shown in Figure 1. Complex (**1**) can be reduced reversibly ($E^{0\prime}$ = −0.91 V *vs.* Ag/AgCl) by one electron, but the second reduction ($E^{0\prime}$ = −1.38 V) is accompanied by decomposition of the $[(\mathbf{1})]^{2-}$ species. The decomposition product is observed at −0.80 and 0.48 V in Figure 1A. This decomposition reaction can be exaggerated by holding the applied potential at −1.8 V for 30 s before initiating the reverse, positive scan (Figure 1B). The decomposition of $[(\mathbf{1})]^{2-}$ can be achieved chemically by the addition of excess sodium naphthalenide to a C_6H_6 solution of (**1**) to yield a diamagnetic, monophenyl complex (^{1}H NMR). The neutral monophenyl complex (**2**) can be obtained from the purification of (**1**) by adding THF (2 v/v% in final eluent) to C_6H_6/hexanes eluent after the main product has eluted or by reacting PhLi with $[Ru_2(OEP)_2](BF_4)_2$.[7] ^{1}H NMR (Table 1) reveals that (**2**) is paramagnetic and that THF is an axial ligand; for simplicity we shall omit writing the THF ligand. The cyclic voltammetric response of (**2**), shown in Figure 1C, reveals a one electron reduction couple at −0.8 V that matches precisely that of the decomposition product of $[(\mathbf{1})]^{2-}$. The voltammetry, chemical reductions, and NMR indicate that the decomposition product is the reduced $[(\mathbf{2})]^-$ form (Table 1), which can be prepared independently by addition of sodium naphthalenide to $[(\mathbf{2})]$. These observations are incorporated into Scheme 1.

The cyclic voltammetric response of (**1**) shown in Figure 1A also reveals an irreversible oxidation ($E_{p,a}$ = +0.73 V and $E_{p,c}$ = +0.04 V). Oxidation of a C_6H_6 solution of (**1**) with $AgBF_4$ yields a paramagnetic solid whose ^{1}H NMR spectrum is consistent with the *N*-Ph complex $[(\mathbf{1})$-*N*-OEP$]^+$. $[(\mathbf{1})$-*N*-OEP$]^+$ exhibits voltammetric waves identical to those of (**1**), so the *N*-dearylation step must be rapid, likely through a square scheme[3] as shown in Scheme 1. Unlike with (**1**), the oxidation of (**2**) ($E^{0\prime}$ = +0.48 V) with $AgBF_4$ leads to the stable, paramagnetic (Table 1) cation $[(\mathbf{2})]^+$ that does not *N*-arylate. This is in contrast to that anticipated from the corresponding Fe(TPP)(Ph) (TPP = tetraphenylporphyrin dianion) chemistry.[3] We are encouraged by these preliminary results, since the reactions appear simple and the products are easily purified and characterized. We are eager to extend these studies to other aryl and alkyl complexes,[6—9] for they may provide an interesting comparison to the known chemistry of related organometallic porphyrins.[1—2]

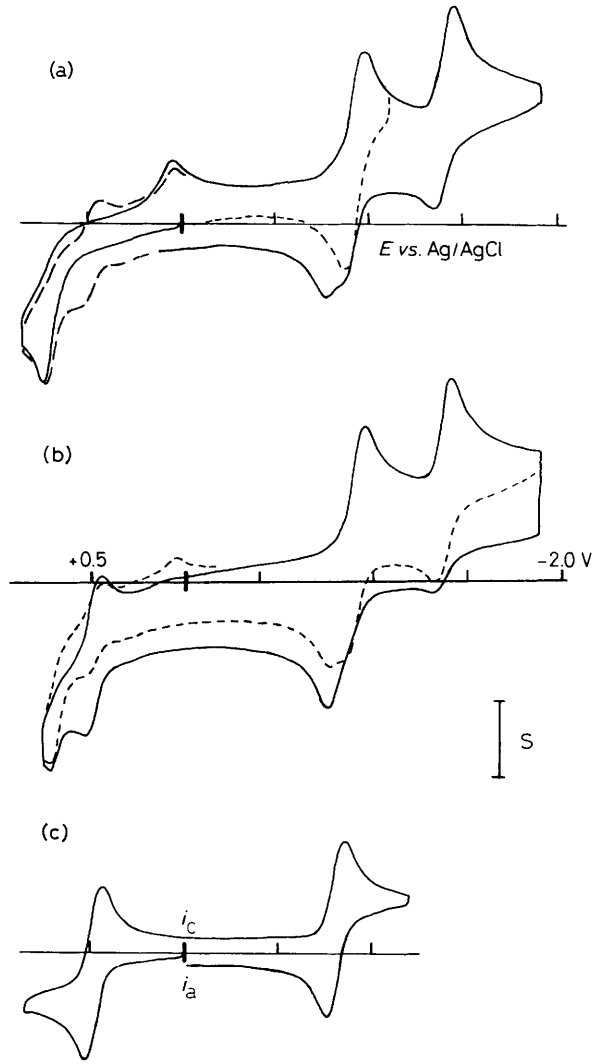


Figure 1. The cyclic voltammetric response of the Ru(OEP)(Ph) complexes in 0.2 M Bu_4ClO_4/THF at a Pt disc electrode (0.08 cm^2) at 200 mV s^{-1}. (a) (**1**), scan initiated in positive direction from 0 V, S = 5 μA cm^{-2}. (b) (**1**), scan initiated in negative direction from 0 V; (---) continuous reverse scan; (——) applied potential held at −1.8 V for 30 s before initiating the reverse scan. (c) (**2**), scan initiated in positive direction from 0 V, S = 10 μA cm^{-2}. All potentials *vs.* Ag/AgCl; ferrocene/ferrocenium couple is observed at +0.43 V *vs.* Ag/AgCl.

Table 1. ^{1}H NMR chemical shifts (δ) for Ru(OEP)(Ph) complexes.[a]

Complex	Me	CH_2	H_{meso}	(Ru)Ph
(**1**)	1.73	3.68	9.92	5.02, 4.82, 1.17
[(**1**)-*N*-OEP]$^+$	−0.91, −0.43 2.28, 3.39	−1.25, 1.34,[b] 4.91 7.47, 13.96, 28.29 12.01	−12.3,[c] −1.0[c]	48.88, 44.2, 10.47 8.48, −106.8, −130.2[c]
(**2**)[d]	−1.23	13.44, 5.80	0.35	49.9, −47.5, −81.8
[(**2**)]$^-$	1.83	3.70	8.96	4.98, 4.76, 2.61
[(**2**)]$^+$[e]	7.61	85.9, 56.8	28.1	72.8, −186.4, −208.7

[a] All spectra were obtained on a 200 or 300 MHz instrument in C_6D_6, except for [(**2a**)]$^+$ and [(**1**)-*N*-OEP]$^+$ in CD_2Cl_2. [b] 4H. [c] These chemical shifts cannot be assigned unambiguously to the Ru–*Ph* or *N*–OEP–*Ph* groups. Further NMR experiments are underway to resolve this issue. [d] Co-ordinated THF observed at δ 4.41 and 11.42. [e] Co-ordinated THF observed at δ 9.6 and −5.9.

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