Reversible Intramolecular Electron Transfer within a Ruthenium(III) Porphyrin–Ruthenium(II) Porphyrin π-Cation Radical System induced by Changes in Axial Ligation

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Reaction of the octaethylporphyrinatobis(triphenylarsine)ruthenium(III) cation with CO generates the carbonyl(triphenylarsine)ruthenium(II) porphyrin π-cation radical species *via* an intramolecular electron transfer; the process is quantitatively reversible.

We have reported recently on intramolecular electron transfer from the metal centre of ruthenium(II) porphyrin π-cation radicals to the porphyrin ring [equation (1), OEP = dianion of octaethylporphyrin],[1] and now wish to describe the reverse of such a reaction within the L = $AsPh_3$ system which shows complete reversibility as a function of axial ligation [equation (2)].

$$\{[Ru^{II}(OEP^{+\bullet})(CO)]^{+}X^{-}\} + 2L \rightarrow$$

X = vacant (1) or Br

$$[Ru^{III}(OEP)L_2]^{+} + CO + X^{-} \qquad (1)$$

(2) L = PPh_3
(3) L = $PBu^n{}_3$

$$\underset{(4)}{[Ru^{III}(OEP)(AsPh_3)_2]^{+}} + CO \rightleftharpoons \underset{(5)}{[Ru^{II}(OEP^{+\bullet})(CO)(AsPh_3)]^{+}} + AsPh_3 \qquad (2)$$

Addition of two equivalents of $AsPh_3$ to a 10^{-4} M solution of (1) (which exhibits an $^{2}A_{2u}$ ground state[1,2]) in CH_2Cl_2, followed by purging with argon to remove CO, generates a bright orange solution of (4) that has an optical spectrum ($\lambda_{max.}$ 396, 518, 810 nm) similar to those of (2) and (3). Treatment of (4) with CO at 1 atm. generated a new radical species (5). E.s.r. studies at 77 K showed (5) to be a porphyrin π-cation radical ($g_{av.}$ centred at 2.004) which exhibited a 4-line spectrum ($A_{\parallel}$ *ca.* 35 G, $A_{\perp}$ *ca.* 2 G) due to coupling to co-ordinated arsine (^{75}As, I = 3/2, 100% abundance); the optical spectrum of (5) ($\lambda_{max.}$ 587,610 nm) is again typical of an $^{2}A_{2u}$ ground state.[1,3] Purging this solution of (5) with argon regenerated (4), and this reversibility could be repeated with close to 95% yield in either direction. Solutions of (4) were also generated electrochemically from $[Ru(OEP)(AsPh_3)_2]$† in 0.05 M Bu_4NClO_4–CH_2Cl_2 ($E_{1/2}$ = 0.18 V, *vs.* Ag/AgCl): carbonylation gave (5) but also *ca.* 30% reduction to [Ru(OEP)(CO)] ($\lambda_{max.}$ 392, 512, 547 nm)[1] and to $[Ru(OEP)(CO)(AsPh_3)]$ ($\lambda_{max.}$ 406, 525, 554 nm)[3] was noted.

Further examples of electron transfer from porphyrin to metal are shown by analogous phosphine complexes, but the reactions are less clean. Thus a CH_2Cl_2 solution of (2), that is in equilibrium with the five-co-ordinate species $[Ru^{III}(OEP)(PPh_3)]^{+}$,[4] reacts readily with CO to give finally an equilibrium mixture of the reduction products [Ru(OEP)(CO)] and $[Ru(OEP)(CO)(PPh_3)]$, as judged by optical spectral data;[1] however, an observed green intermediate ($t_{1/2}$ *ca.* 10 min) with $\lambda_{max.}$ 610 nm is almost certainly the cation-radical species $[Ru^{II}(OEP^{+\bullet})(CO)(PPh_3)]^{+}$,[1,4] strongly suggesting an initial reaction comparable to equation

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† This complex has been isolated in the solid state and fully characterized by elemental analysis and n.m.r. and mass spectral data (ref. 3).

(2). The nature of the subsequent reduction process, like that sometimes noted with (**5**) (see above), will be discussed elsewhere and probably involves disproportionation of the cation-radical to give a reduced product and a dication that is even more readily reduced by solvent or impurities.[5] A corresponding treatment of $[Ru^{III}(OEP)(PBu^n_3)]^+$‡ with CO similarly gives initially $[Ru^{II}(OEP^{+\bullet})(CO)(PBu^n_3)]^+$ ($\lambda_{max.}$ 630 nm) that, if kept under CO, slowly undergoes the ligand transfer reaction shown in equation (3).

$$2[Ru^{II}(OEP^{+\bullet})(CO)(PBu^n_3)]^+ \rightarrow \mathbf{(3)} + \mathbf{(1)} + CO \qquad (3)$$

In the presence of excess of phosphine or arsine, which maintains the six-co-ordinate $Ru^{III}(OEP)L_2$ species in solution,[4] reactivity toward CO is strongly inhibited, showing as expected that dissociation of an axial ligand is a key initial step in the CO-promoted intramolecular electron transfer. That CO stabilizes the Ru^{II} state with respect to Ru^{III} within porphyrin systems is well-documented,[1,6] but direct evidence for electron transfer from the porphyrin ligand to a metal initiated by axial ligand substitution within any system has previously been lacking. A corresponding process within Ni^{III}/Ni^{II} porphyrin and other macrocycle systems, that involved a temperature-dependent internal electron transfer, had been suggested to result from axial ligation, but in each case electron transfer to the metal was associated with a solid (77 K) to solution phase change.[7]

The nature of the axial ligand(s) within ruthenium porphyrin systems can clearly regulate electron transfer in both directions between metal and porphyrin, equation (2), and such substitution processes will almost certainly play a key role within heme protein cytochrome systems.[8]

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‡ Species generated *in situ* by one-electron oxidation of $[Ru(OEP)(CO)(PBu^n_3)]$ (ref. 1) to $[Ru^{II}(OEP^{+\bullet})(PBu^n_3)]^+$ ($E_{1/2}$ = +0.59 V), followed by purging with argon to remove the CO, (ref. 3) *cf.* equations (1) and (2).

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