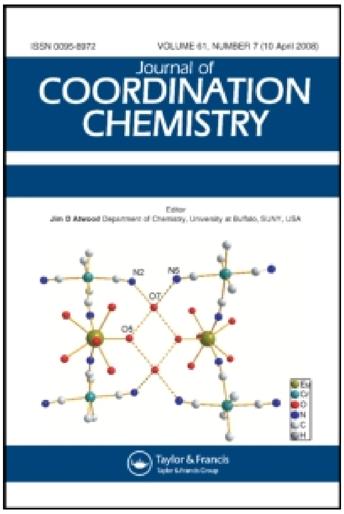

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SHORT COMMUNICATION
An Electrochemical Investigation of some Rhenium Carbonyl Porphyrins

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Cyclic voltammetric studies of $[Re(CO)_3]_2$TPP and $[Re(CO)_3]$H—TPP were carried out in an attempt to verify the previously proposed formation of an Re—Re bond by chemical oxidation. This study indicates that the first oxidation step of both complexes is similar, but the next oxidation step is very different. However, the first product species are very similar. We conclude that electrochemical oxidation of the $[Re(CO)_3]$H—TPP is accompanied by a chemical rearrangement leading to formation of a species containing two Re atoms connected by at least a partial Re—Re bond.

Sir:

Earlier reports[1,2] described the synthesis and x-ray crystallographic characterization of mono- and di-rhenium carbonyl prophyrins. The x-ray data indicated that in some cases an inter-molecular rhenium-rhenium bond was formed as a result of chemical oxidation. We wish to report electrochemical evidence which tends to confirm the formation of such a metal-metal bond.

The use of cyclic voltammetry to probe the energy levels of metal complexes and to investigate the stability of the resulting oxidation and reduction states is well established[3,4]. The cyclic voltammetric studies were carried out on a locally constructed instrument, the details of which will appear elsewhere. The three-electrode electrochemical cell is similar to the form developed by VanDuyne,[5] having a Lugen probe for the reference electrode. This allows placement of the probe tip within 1 mmof the working electrode, thus minimizing solution resistance effects. The auxiliary electrode is a platinum wire concentrically wound around a glass rod containing an axially mounted 4 mm platinum wire used to form the working electrode. The rod was end polished and the electrode buffed between experiments with Whatman #42 filter paper to eliminate film formation. The reference electrode was a silver–silver perchlorate in acetonitrile system with an asbestos fiber wick junction to the working solution. Vacuum-dried electrochemical grade tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte. The complexes were prepared as previously described.[6] The solvent was spectroscopic grade dichloromethane. All solutions were 0.30 M. in TEAP and 1 millimolar in complex or H_2TPP. The solutions were deoxygenated by saturation with purified nitrogen. The gas was passed through a three stage drying train to remove water and then through a scrubbing tower filled with supporting electrolyte solution. This final step was necessary to presaturate the gas stream and minimize concentration changes caused by evaporation of solvent from the samples.

The electrochemical results obtained for three *meso*-tetraphenylporphine, H_2TPP, [monohydrogen meso-tetraphenylporphinato] tricarbonylrhenium(I), $(Re(CO)_3HTPP)$, **1**, [*meso*-tetraphenylporphinato]-bis[tricarbonylrhenium(I)], $(Re(CO)_3)_2$TPP, **2**, and *meso*-tetraphenylporphinato cobolt(II), CoTPP, are shown in Figure 1 as curves A, B, C and D respectively. CoTPP is included as a reference compound because its electro-chemistry has been studied previously in this media.[7]

The free H_2TPP, mono- and di-rhenium compounds all exhibit two consecutive, chemically stable, one electron reductions with peak potentials of −1.52 and −1.83 V for H_2TPP (curve A), −1.41 and −1.74 V for (**1**), and −1.20 and −1.54 V versus reference for (**2**), CoTPP shows a chemically stable, reversible one electron transfer process at −1.00 V, but a second reduction (not shown) near −1.60 V leads to a chemically unstable product under these conditions. The chemical kinetics involved can be outrun by using sweep rates in excess of 10 V/s. The reductive electrochemical behavior is unremarkable, exhibiting

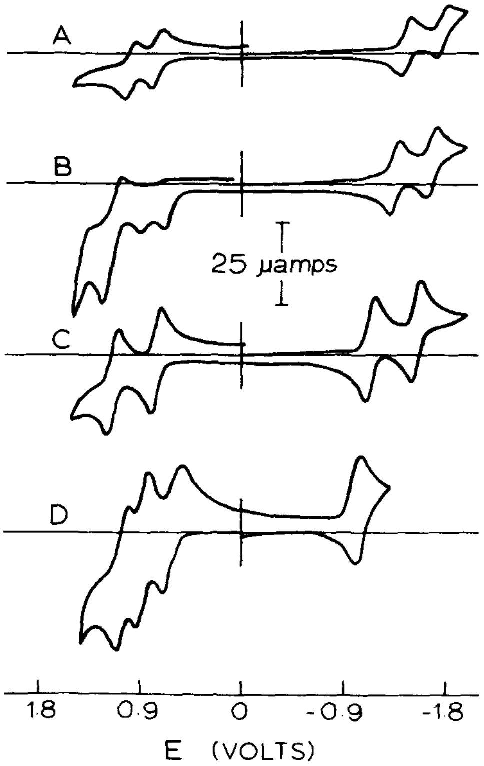

FIGURE 1 Cyclic voltammograms in 0.1 M TEAP at a platinum electrode of (a) H_2TPP, (b) $[Re(CO)_3]$ HTPP, (1), (c) $[Re(CO)_3]_2TPP$, (2), and (d) CoTPP. Scan rate, 0.1 V/S.

the expected lowering of energy levels of the first available orbitals as one proceeds from H_2TPP to the mono- and di-rhenium species.

The oxidative electrochemistry of these species is somewhat more complex. Oxidation of H_2TPP occurs in two consecutive one-electron steps at 1.04 and 0.80 V and both product species are stable in solution on the time scale of the experiment (curve A). The di-rhenium complex (2) (curve C) also shows consecutive one-electron oxidation at 0.81 and 1.22 V versus reference. Oxidation of CoTPP is in accord with the results of other workers[7], with the Co(II) → Co(III) oxidation occuring at 0.57 V and the two ligand oxidations occuring at 0.96 and 1.14 V (curve D). Oxidation of the mono-rhenium species (2) shows an oxidation process whose peak potential occurs at 0.68 V at a sweep rate of 0.1 V/s. The resulting oxidation product is chemically unstable on this time scale although some indication of a re-reduction can be seen.

A second oxidation occurs at about 0.90 V and the product is even less stable in solution. Both oxidations exhibit a peak current which is essentially identical to that found for the reductions indicating that both are probably one-electron processes. At more positive potentials a further oxidation occurs at 1.22 V versus reference. This product is *stable* on the time scale of the experiment, while the amount of current obtained is consistent with a two-electron oxidation. Increasing the sweep rate shifts the first wave more anodically and increases the re-reduction current although a shape characteristic of a stable chemical species was not obtained at sweep rates up to 50 V/s where a peak potential of about 0.74 V was observed. The second charge-transfer process is affected very little by the increased sweep rate. Because it was not possible to outrun the chemical kinetic processes involved in the first two oxidations, one can not state the corresponding oxidation potentials precisely, but one can set lower limits of 0.74 and 0.95 V versus reference repectively on the basis of the high sweep rate studies.

The correspondence of the first oxidation potential for H_2TPP and 2 would seem to indicate that the orbitals involved both come from the ligand moiety and contain very little metal character. The second oxidation of 2 involves an orbital having a fair degree of metal character as evidenced by the 0.18 V shift in potential. There are several interpretations for the observed electrochemical behavior of **1**. One can argue that the first oxidation corresponds to the first process observed in 2 but that the oxidized species then decomposes due to a localized charge defect which is not found in either 2 or H_2TPP. This charge defect could be on the rhenium atom or on the porphyrin ligand. If the site of the defect was interior to the ring structure, it would be shielded by the rhenium atoms in 2. In conjunction with the x-ray crystallographic data, it seems more likely that the charge defect is on the rhenium atom since 2 shows evidence of an existing metal–metal bond which would tend to stabolize the oxidation product of 2 relative to **1**. The correspondence between the final oxidation potentials of both 1 and 2 indicates that the electrons involved come from orbitals of very nearly the same energy, while the relative stability of the two oxidized species indicates that the moieties have similar chemical properties in the experimental environment. These observations, in conjunction with the two electron transfer involved in the final oxidation of 1 make it tempting to speculate that the chemical rearrangements involved lead to a dimerization of 1 with the formation of at least a partial rhenium–rhenium bond.

This hypothesis is merely speculative at this time but it is consistent with the available data. Further studies involving bulk electrolysis and spectro-electrochemical techniques are in progress in an attempt to clarify the situation.

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