Hence this provides *the direct observation of the π-allyl-hydride exchange mechanism* proposed for 1,3 hydride shifts found in many metal catalyzed olefin reactions.

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(4) Pyrolysis (>100°) or reaction of **1** with CO, N_2, or TCNE yielded only C_2H_4; with Br_2, C_2H_4 and $C_2H_4Br_2$ were produced. In reactions at 25° with excess HCl or CF_3COOH both C_2H_6 and C_2H_4 are evolved.
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Electron-Transfer Reactions in Metalloporphyrins

Sir:

This report describes some experiments concerning electron-transfer reactions with metalloporphyrins that demonstrate that the path of electron transfer to the metal ion center can be via the porphyrin π-cloud and not via the fifth and sixth metalloporphyrin ligand positions.[1-4]

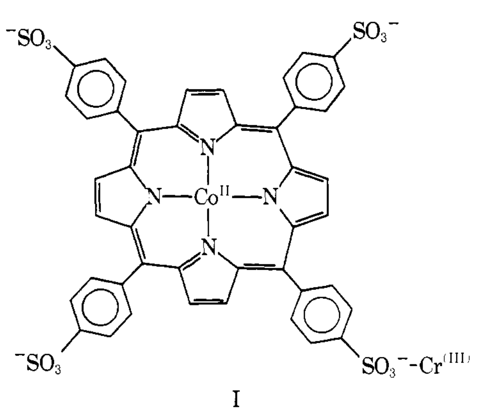
The reduction of the water-soluble tetra[*p*-sulfonatophenyl]porphinatocobalt(III), Co(III)-TPPS,[5-7] by chromous ion leads to the below rate law which is similar to the previously observed rate laws for the reduction of metalloporphyrins.[1,2,8]

$$\text{rate of reduction} = \{k_1/[H^+] + k_2[Cl^-] + k_3[SCN^-]\}\,[Cr^{2+}][Co^{III}TPPS]$$

The rate constants in the above equation evaluated at 30° and an ionic strength of 0.25 ($NaClO_4$) are $k_1 = 4.9$ sec^{-1}, $k_2 = 2.9 \times 10^4\ M^{-2}$ sec^{-1}, and $k_3 = 1.3 \times 10^6\ M^{-2}$ sec^{-1}. The results are valid between pH 1.0 and 5.0.[9]

Since the rate of Co^{III}TPPS-SCN formation is slower than the electron transfer[10,11] a bridged Co(III)-N-C-S-Cr(II) reaction pathway can be ruled out. This is in agreement with the studies of Pasternack and Sutin.[2]

To further probe the mechanism of this reaction a product study was carried out which demonstrates that the reaction products have the Cr(III) bound to the Co(II)-TPPS moiety. This was verified by carrying out the reaction under stoichiometric conditions employing ^{51}Cr as a tracer[12] and using cation exchange columns to separate the products.[14]



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We infer that the Cr(III) is attached to the sulfonate group as shown in structure I. These experiments imply that the electron-transfer goes via the porphyrin π-cloud and not via the fifth and sixth position[15] and also clearly demonstrate that the anion effects in these metalloporphyrin reductions are due to nonbridging ligand effects.

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(8) Our rate does differ in one respect from that of Sutin and Pasternack in that we have a zero intercept in the plot of $k_{obsd}/[Cr^{2+}]$ vs. $1/[H^+]$.
(9) The reactions were run under pseudo-first-order conditions in a Durrum–Gibson stopped-flow machine with Co(III)–TPPS concentration about 1×10^{-5} *M* and $[Cr^{2+}]$ at $(3\text{–}6) \times 10^{-3}$ *M*. The wavelengths at both 427 and 411 nms were employed to follow the course of the reaction.
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(11) The rate constant k_3 is the same whether the SCN^- is placed with the Co(III)–TPPS solution or the Cr^{2+} solution.
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(14) A stock solution of $^{51}Cr^{III}(H_2O)_6^{3+}$ (1949 (counts/min)/10 ml of 9×10^{-5} *M* solution) was employed in these experiments. If 10.0 ml of the above solution was passed through an ion exchange column of Dowex 50W-X8 (9 × 1 in.) the eluent collected had an activity of 249 counts/min. A blank water solution had a counting rate of 236 counts/min. Thus the ion exchange resin caught 99% of the $Cr(H_2O)_6^{3+}$. If an equimolar mixture of $^{51}Cr(H_2O)_6^{3+}$ and Co(III)–TPPS was passed through the column the porphyrin containing eluent had a counting rate of 267 counts/min. On the other hand, when an equimolar mixture of $^{51}Cr(H_2O)_6^{2+}$ (produced by Zn(Hg) reduction of the radioactive chromic solution) and Co(III)–TPPS was passed through the column the porphyrin containing eluent now had a counting rate of 1951 counts/min. Thus the products of the reaction of chromous ion with the cobaltic porphyrin (chromic and cobaltous porphyrin) were completely eluted off the column. This demonstrates that the chromic ion is bound to the metalloporphyrin via the electron-transfer reaction. Interestingly, one can reoxidize the Cr(III)–Co(II)–TPPS with ferricyanide to the Cr(III)–Co(III)–TPPS and rereduce (with a different rate) the Co(III) center with $Cr(H_2O)_6^{2+}$ and isolate a $[Cr(III)]_2$–Co(II)–TPPS product.
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Nickel-Promoted Synthesis of Cyclic Biphenyls. Total Synthesis of Alnusone Dimethyl Ether

Sir:

Organotransition metal complexes are appearing with increasing frequency in synthetic methodology and in com-