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Richard H. Fish

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### ACCEPTED MANUSCRIPT

### 2014 International Award Paper for Achievements in Bioorganometallic Chemistry

# A Bioorganometallic Chemistry Perspective: Organometallic Chemistry at the Interface with Biology

#### Richard H. Fish\*

Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94708, USA

**Abstract:** A 41 year perspective on our bioorganometallic chemistry studies that included reactions of organotin compounds with cytochrome P450 enzymes, and their biomimics; identification of natural organoarsenic compounds in oil shale; reactions of an Cp\*Rh tris aqua complex with nucleobases; supramolecular Cp\*Rh-nucleobase complexes in host-guest chemistry; chemoselective reduction of NAD<sup>+</sup> biomimetic cofactors with an Cp\*Rh-hydride to provide 1,4-NADH biomimics, in tandem with enzymatic catalysis for stereoselective reductions of achiral ketones to chiral alcohols, and including oxidation reactions with cytochrome P450 enzymes; synthesis and bioassays of organorhodium-hydroxytamoxifen breast cancer pharmaceuticals; and synthesis and bioactivity of Cp\*Rh-G-Protein Coupled Receptor peptides, will be presented in this 2014 ISBOMC Award Paper.

Introduction: Bioorganometallic Chemistry Projects at Lawrence Berkeley National Laboratory, University of California, Berkeley, and with other Collaborators from 1973-2014.

For many years, I had been interested in adding a biological component to my organometallic chemistry research projects. After my PhD in organotin hydride reactions with allenes/dienes in 1965, I initially began my career in the chemical industry conducting studies on organoboron chemistry, 1965-1967, and then as a Postdoctoral/Lecturer in Chemistry at the University of California, Irvine in 1968-1969, conducting photochemical research. From 1970 to 1973, I took a position at a US Department of Agriculture Laboratory in Berkeley, CA, and was focused on environmental organometallic mercury chemistry, where  $Hg^{2+}$  was reacted with  $\beta$ -diketones to provide a new class of C-Hg  $\beta$ -diketones complexes; at that time,  $Hg^{2+}$  and  $CH_3HgX$  complexes were being found in seafood, and were also environmental toxins in water. It is important to remember that methyl-B12 biomethylates many toxic metal; for example, Hg, Sn, As, Se, etc., and the  $CH_3$ -M analogues of these inorganic metals were found to be extremely more toxic than their inorganic metal counterparts, to humans.

In 1973, I was invited to collaborate on a NIEHS grant on the UC Berkeley campus, with a focus on the metabolism of tributyltin derivatives with cytochrome P450 enzymes, since these organotin compounds were being sprayed on food products for pest control. This latter project provided me with a new direction, Bioorganometallic Chemistry, and at the interface with Biology. In this ISBOMC'14 award paper, I will start from 1973, and peruse the Bioorganometallic Chemistry projects we have conducted up to the present at LBNL/UC Berkeley, and with colleagues around the globe.

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