IRIDIUM CORROLES: SYNTHESIS, PROPERTIES, AND ELECTRONIC STRUCTURE

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ABSTRACT

The synthesis, properties, and electronic structures of a family of iridium corrole complexes are discussed in detail. These compounds represent the first well-characterized examples of third-row metals being inserted successfully into the small corrole binding pocket; they possess a planar macrocycle, which neither saddles nor ruffles upon bromination, and are bound at the axial positions by either two amine ligands or one phosphine. Unlike their well-studied cobalt and rhodium analogues, whose redox activity is restricted primarily to the corrole ring, iridium corroles can be oxidized to produce an electron paramagnetic resonance spectrum that has extremely anisotropic g tensor components, implying mixing of the 5d orbitals into the oxidized ground state and opening the door to possible higher-valent iridium complexes. Detailed experimental and computational studies are presented showing that this oxidized ground state is actually mostly corrole-based, as has been found in the past for numerous other supposedly high-valent corrole compounds, but the percentage of iridium character varies from 10 to 18% and tracks with the electron-donating ability of the ligand. Additionally, the unique (among corrole complexes) near-IR phosphorescence of Ir(III) corroles is presented and discussed. Iridium(III) corroles phosphoresce with lifetimes ranging from hundreds of nanoseconds to a few microseconds at room temperature, with slightly longer lifetimes at low temperature. Unfortunately, the quantum yields of phosphorescence are low, 1% or less, and this appears to be due to an exceptionally slow set of radiative rates for the corroles. An examination of the reactivity of ammine-ligated Ir(III) corroles is also described. These compounds can be oxidized in the presence of an ammonia source to form novel six-coordinate iridium(III) azaporphyrins in an unprecedented chemical transformation. The characterization and properties of these iridium azaporphyrin complexes are detailed as well, with a focus on nuclear magnetic resonance characterization techniques and a discussion of the red phosphorescence of the azaporphyrins.

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NOMENCLATURE AND ABBREVIATIONS

BILRC Beckman Institute Laser Resource Center

bpy 2,2’-bipyridine

btfmpy (bis)-3,5-trifluoromethylpyridine

dcpy 3,5-dichloropyridine

cnpy 4-cyanopyridine

cod 1,5-cyclooctadiene

COSY correlation spectroscopy

CV cyclic voltammetry, cyclic voltammogram

dcm dichloromethane

DFT density functional theory

dmap 4-(N,N-dimethylamino)pyridine

edta ethylenediaminetetraacetic acid

ESI electrospray ionization

HMBC heteronuclear multiple-bond correlation

HSQC. heteronuclear single-quantum correlation

HOMO highest occupied molecular orbital

HPLC high-performance liquid chromatography

H_3tpfc 5,10,15-(tris)pentafluorophenylcorrole (tpfc is the trianionic form)

H_3tfc 5,10,15-trifluorocorrole (tfc is the trianionic form)

IC Inorganic Chemistry (journal)

ISC inter-system crossing

JACS Journal of the American Chemical Society

meopy 4-methoxypyridine

MS mass spectrometry

NBS N-bromosuccinimide

NMR nuclear magnetic resonance

ppm parts per million

py pyridine

SCE saturated calomel electrode

SOMO singly occupied molecular orbital

SSRL Stanford Synchrotron Lightsource

***t*-4bpa** (tris)(4-bromophenyl)ammoniumyl hexachloroantimonate

tma trimethylamine

TLC thin-layer chromatography

XAS X-ray absorption spectroscopy

Opening Remarks

A BRIEF INTRODUCTION

I'm an inveterate experimentalist, and for better or for worse, this thesis has come to reflect that. It is split into a large number of bite-sized chapters, much like my research here at Caltech, and I hope that the end result proves refreshing rather than disorienting. Harry Gray, my graduate supervisor, advised me to reformat rather than rewrite my published work, and the first four chapters of the thesis are published work presented here in essentially the same form as they have been presented to the larger scientific community (with some additional notes, changes to figures, formatting, and nomenclature for consistency between chapters, and introductory statements added in for flavor, background, and feel). The papers discussed herein include: my first JACS communication, "Iridium Corroles" (DOI: 10.1021/ja801049t); a detailed electronic structural study from IC entitled "Structures and Reactivity Patterns of Group 9 Metallocorroles" (DOI: 10.1021/ic901164r); another JACS communication focusing on corrole photophysics, "Near-IR Phosphorescence of Iridium(III) Corroles at Ambient Temperature" (DOI: 10.1021/ja101647t); and a computational study from IC, very recently published and performed in collaboration with members of Bill Goddard's group, entitled "Electronic Structures of Group 9 Metallocorroles with Axial Ammines" (DOI: 10.1021/ic1005902).

Additionally, two pieces of unpublished work will be presented. These include a description of some unique reactivity of an easily oxidized Ir(III) corrole complex, which will be presented as if it were a journal article, and a combined DFT, EPR, and XAS study of the electronic structures of a host of iridium corroles, which is less close to completion and will be discussed only briefly. I have attempted to present these unpublished studies in a similar fashion to the published ones, but these latter chapters may have a slightly more informal tone in keeping with my own stylistic tendencies. I hope they will provide an interesting and informative read nonetheless.