Aspects of Organometallic Chemistry, Particularly Metal Alkynyl and Cluster Chemistry

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Table of Contents

Abstract
Statement
Acknowledgements
Curriculum vitae
List of publications in chronological order
List of publications classified by research field
Outline of the research, the significance of the publications, and percentage contributions
Copies of publications arranged in chronological order
Abstract

The research presented for the degree of Doctor of Science largely comprises contributions to organometallic chemistry, focusing on two major areas: the nonlinear optical (NLO) properties of metal acetylides (metal alkynyl complexes), and aspects of cluster chemistry.

The studies of the NLO properties of metal alkynyl complexes summarized herein have demonstrated that metal alkynyl complexes can be designed to have very large molecular NLO coefficients. This work involved the development of structure-NLO property relationships. Specifically, the research demonstrated the importance of metal valence electron count, ease of oxidation, nature of co-ligand, a variety of alkynyl ligand modifications, and chain-lengthening of alkynyl ligand by various bridging units upon quadratic and cubic NLO responses. These studies also demonstrated the utility of spectroscopic, electrochemical and computational aids as predictive tools for efficient NLO materials. In the process, the organometallic complexes with the largest quadratic and cubic optical nonlinearities to that time were prepared.

To extend these NLO studies of alkynylmetal complexes from dipolar to octopolar and dendritic compounds, syntheses of a new class of complex, namely alkynylruthenium dendrimers, were developed. These syntheses were initially by classical (organic) convergent methods, and subsequently utilizing "steric control" to rapidly prepare the requisite dendrons. Large cubic nonlinearities in novel quadrupolar, octopolar and dendritic alkynylruthenium complexes were demonstrated (the first for any molecular compounds without appreciable charge asymmetry), these studies showing that n-delocalized organometallic oligomers and dendrimers can have extremely large two-photon absorption cross-sections; values of the same order of magnitude as the best organic materials, but without introduction of strongly polarizing substituents which reduce optical transparency.

These studies also resulted in the first demonstration of photo switching of optical nonlinearity in organometallic complexes, the first demonstration of electrochemical switching of optical nonlinearity, the first electrochemical switching of cubic nonlinearity, and the first switching of nonlinear absorption in any molecular material. The first application of electroabsorption spectroscopy to determine nonlinearities of organometallics was reported as a result of these studies. These investigations of the NLO properties of alkynylmetal complexes over the past decade have demonstrated that organometallics can have comparable NLO efficiencies to the best organic materials, but possess additional advantages due to their more facile switching between two states with differing (\textcolor{red}{\textbf{+ve/-ve or ON/OFF}}) NLO responses.

Also summarized herein are studies of the NLO properties of inorganic, organic and organometallic compounds, and syntheses of a range of precursor compounds and related studies.

The second major focus of the research presented for the degree of Doctor of Science is cluster synthesis, reactivity and physical properties. The research with ruthenium clusters and hard-donor (N, O) ligands afforded a series of cluster complexes...
incorporating piperidine, pyridine and phenol residues in varying coordination modes 
that provide structural models for industrially important hydroprocessing intermediates. 
The studies also led to the development of facile high-yielding syntheses of high-
uncertainty clusters, crystallographic studies showing conclusively that the hydrido 
ligand is external to the decametallic core rather than occupying the tetrahedral “hole” in 
the cluster skeleton as had been previously assumed. The decaruthenium clusters 
exhibit step-wise reactivity towards nucleophiles under exceptionally mild conditions. 
Spectroscopic, magnetic and computational techniques were employed to show that 
these clusters are molecular rather than “mesomeric” in character, overthrowing the 
existing dogma, and the electrochemical behaviour of these clusters was examined. 
Ruthenium cluster units have also been incorporated into “star” molecules.

A systematic study of group 6-iridium clusters, which is also described herein, involved 
the synthesis of almost all of the extant mixed molybdenum-iridium and tungsten- 
iridium clusters. The research focus has been the series M2(Ir0.4xCO)2.4x(N3-L)2 (M = 
Mo, W; L = various cyclopentadienyl ligands; x = 0-2), which was utilized to assess the 
effect of disparate metal incorporation and replacement upon structure, reactivity, 
fluxibility, and other physical properties. These investigations revealed enhanced 
reactivity towards nucleophiles, enhanced activation of coordinated ligands, differing 
base-promoted cluster condensation pathways, and differing CO flexibility for the 
mixed-metal clusters compared to the isobal homometallic cluster Ir6(CO)12. A 
progression to linked clusters has afforded cluster dimers, trimers, oligomers, and 
dendrimers. The electrochemical properties of these clusters are tuned by systematic 
ligand substitution, and modified upon linking clusters by π-stabilizable bridges.