Spectroscopic investigation of di-u-hydroxo bridged platinum complexes
by John Raymond Marvin

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University

Abstract:
When various Pt(II) complexes, coordinated in a cis fashion by certain monodentate sulfoxide and phosphane ligands, undergo hydrolysis, an extremely acidic (pH ~ 1.5-2.5) solution results. These hydrolysis reactions are accompanied by the formation of di- and occasionally tri-hydroxo bridged complexes which exist in equilibrium with the monomers at these low pH values. For the sulfoxide complexes, rapid scrambling of the sulfoxide ligands occurs between the two homodimeric forms in solution. The phosphane ligands, in contrast, appear to be considerably more substitutionally inert.

When monodentate sulfoxides are replaced by the bidentate sulfoxide ligand CH3-S(O)-CH2CH2-S(O)-CH3 (MSE), hydrolysis is followed by the formation of a complex mixture of products postulated to have a polymeric structure with the MSE ligand in a bridging role.

Heterodimeric structures were obtained when two different monomeric diaqua complexes containing neutral monodentate phosphane ligands were reacted in aqueous solution. Only the monomeric substitution product was observed when one of the monomers contained an anionic ligand (e.g. oxalate). A series of heterodimeric complexes containing the Pt(PMe3)2 fragment were systematically synthesized incorporating neutral nitrogen and sulfur donor ligands.

A novel network silver complex was obtained and characterized. This structure was initially formed as a result of the incomplete removal of Ag(I) ion used to assist in abstraction of chloride ion from the Pt(II) starting material. A crystal structure was acquired which shows the MSE ligand in a bridging mode.

Attempts to determine the acid dissociation constants of the monomeric diaqua complexes by potentiometric titration revealed a titration curve with only a single apparent inflection point, possibly indicating overlapping pKa values. NMR titration of the trimethylphosphane system, plotting 1H chemical shift vs. pH, revealed, two abrupt transitions which were associated with the pKa's of the coordinated water ligands giving values of 6.5 and 9.6 for pKai and pKa2 respectively. The sum of these pK's was compared with the sum of the dimer formation (Kf) and dissociation (Ka) constants which had also been determined by NMR methods. Kf was found to be 2.701 ± 0.050 and Kd was found to be 22.008 ± 0.059.

SPECTROSCOPIC INVESTIGATION OF

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APPROVAL

of a thesis submitted by

John Raymond Marvin

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Edwin H. Abbott — Edwin H. Abbott (Signature) — 6/30/97 Date

Approved for the Department of Chemistry

David M. Dooley — David M. Dooley (Signature) — 6/30/97 Date

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ABSTRACT

When various Pt(II) complexes, coordinated in a *cis* fashion by certain monodentate sulfoxide and phosphane ligands, undergo hydrolysis, an extremely acidic (pH ~ 1.5-2.5) solution results. These hydrolysis reactions are accompanied by the formation of di- and occasionally tri-hydroxo bridged complexes which exist in equilibrium with the monomers at these low pH values. For the sulfoxide complexes, rapid scrambling of the sulfoxide ligands occurs between the two homodimeric forms in solution. The phosphane ligands, in contrast, appear to be considerably more substitutionally inert.

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Heterodimeric structures were obtained when two different monomeric diaqua complexes containing neutral monodentate phosphane ligands were reacted in aqueous solution. Only the monomeric substitution product was observed when one of the monomers contained an anionic ligand (e.g. oxalate). A series of heterodimeric complexes containing the $Pt(PMe_3)_2$ fragment were systematically synthesized incorporating neutral nitrogen and sulfur donor ligands.

A novel network silver complex was obtained and characterized. This structure was initially formed as a result of the incomplete removal of Ag(I) ion used to assist in abstraction of chloride ion from the Pt(II) starting material. A crystal structure was acquired which shows the MSE ligand in a bridging mode.

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INTRODUCTION

The formation of larger and ever more complex structures from simpler precursors has long been one of the primary goals of the synthetic chemist. Until recently, success in this endeavor has belonged almost exclusively to the field of organic chemistry and, although the vast array of carbon chains and rings can hardly be expected to be matched by transition metals, a great deal of progress has been made in the last few years towards increasingly more complex and functional structures containing multiple metal atoms and metal-metal bonds. In the case of carbon, the enormous diversity of structures can be explained in part by the modest size of the carbon atom and its ability to form robust multiple bonds in small molecules. In the words of one eminent chemist; "Carbon does everything well and nothing to extreme" (1).

The chemistry of transition metals on the other hand is dominated by the availability of partially filled *d* orbitals. From the time of Werner at the beginning of the century up until the early 1960's, the properties of transition metal complexes were accounted for entirely in terms of individual metal atoms surrounded by a primary coordination sphere of ligands (2). It was not until the first experiments postulating the existence of a metal-metal bond were reported that the Wernerian concept of transition metal chemistry had to be modified to include a whole new class of

compounds, now referred to as metal cluster compounds. Clusters have since been defined as "a finite group of metal atoms that are held together mainly or at least to a significant extent, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster" (3). It should be emphasized that this definition specifically excludes complexes in which several metal atoms are held together exclusively by bridging ligands.

General Phenomenon of Metal Ion Hydrolysis

In the context of the preceding definition, the current work has focused on a specific class of di-μ–hydroxobridged compounds with a view towards using these species as building blocks for more complex structures. The creation of metal-metal bonds through oxidation of these complexes is expected to be a logical extension of this work but was of only secondary importance to understanding the fundamental chemistry surrounding the formation and reactivity of these dimers and higher oligomers. Because there were no specific "target" complexes in mind at the outset, each experiment was guided by the results of the previous one in an effort to find appropriate ligands with which to study the hydrolysis and polymerization reactions of the monomeric species.

It has long been known that metal ions undergo extensive and often complicated hydrolysis reactions in aqueous solution. Investigations into these species goes back to the pioneering work of N. Bjerrum (4) into the hydrolysis of chromium(III) and the introduction of the concept of "aquo acidity" introduced by Werner and Pfieffer (5, 6). This process can be described as in Figure 1 which depicts the rapid and reversible hydrolysis of mononuclear species of a tri-positive metal ion such as Al(III) or Fe(III).

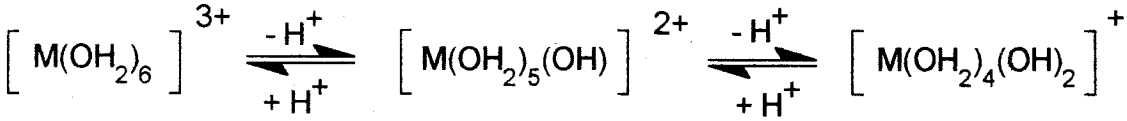

Figure 1. General reaction scheme for the hydrolysis of an aquated metal cation.

The relative strengths of aqua acids have been rationalized in terms of an ionic model which treats the metal ion as a hard sphere with radius **r,** and **z** units of positive charge (7). This model predicts that the acidity of the water in the primary coordination sphere of the metal cation should increase as the value of **r** decreases and as the charge on the metal increases, roughly paralleling the value of the electrostatic parameter given by Equation 1.

Equation 1 $\xi = z^2 / (r + d)$

where **d** is the diameter of the water molecule. This model works well for those metals from groups I and II of the periodic table that normally form ionic solids, but significant deviations are seen for many transition metals due to the departure from purely ionic interactions, as shown in Figure 2.

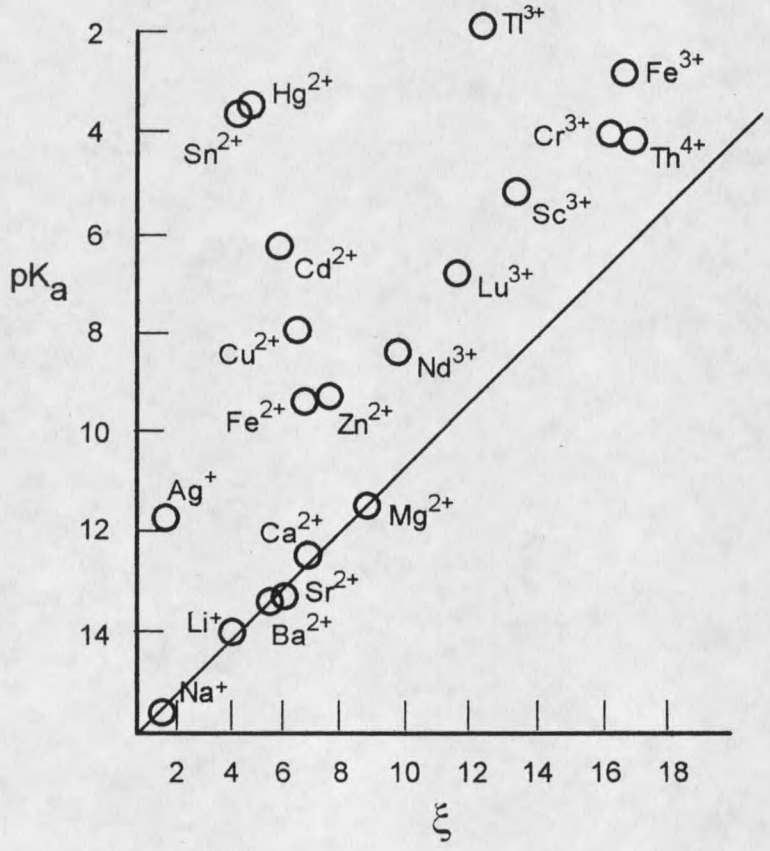

Figure 2. Plot of pK_a vs. electrostatic parameter (ξ) for some metal cations (7).

As the positive charge of the metal ion becomes delocalized over the entire complex, corresponding to a greater degree of covalent character, the proton of the coordinated water is repelled more strongly, resulting in a lower value of pK_a. Although it is probably not safe to extend this reasoning to other metals of the second and third row transition series, it is reasonable to expect that any factors which influence the charge distribution on a metal atom will affect the acidity of coordinated water molecules. Even for metals which do not adhere to this ionic model, the positive charge of the metal ion appears to stabilize the conjugate base of coordinated protic acids (8). The pK_a's for some coordinated protic ligands are given in Table 1 (8, 9).

It has also been firmly established that many hydrolysis reactions are accompanied by polymerization, leading to complex and poorly characterized products. Well known examples include the formation of μ-hydroxo and μ-oxo iron(III) species at intermediate pH. After initial formation of a hydroxo bridge, the pK_a of the bridging hydroxide group is reduced considerably (pK_a=6) by coordination to not just one, but two metal atoms. These metal activated deprotonation reactions are not only important in inorganic systems but also have been postulated as important first steps in some metalloenzyme systems (8). Early studies often failed to recognize these polymerization reactions, resulting in erroneous conclusions concerning formation constants of hydrolysis products.

Table 1. pK_a values for some coordinated protic ligands for the reaction $[MLH]^n$ -----> $[ML]^{n-1} + H^+$ (8, 9)

Metal	Metal Charge/Radius[a]	Ligand	pK_{a1}
-----		H_2O	14.0
Na^+	1.0	H_2O	negligible
Li^+	1.5	H_2O	13.7
Ca^{2+}	2.1	H_2O	13.4
Mg^{2+}	3.1	H_2O	11.4
Zn^{2+}	2.7	H_2O	10.0
Cu^{2+}	2.8	H_2O	10.7
Al^{3+}	6.7	H_2O	5.0
Cr^{3+}	4.8	H_2O	4.0
Fe^{3+}	4.7	H_2O	2.7
-----		NH_3	35.0
Cu^{2+}	2.8	NH_3	30.7
Ni^{2+}	-----	NH_3	32.2
Co^{2+}	-----	NH_3	32.9

a) Relative to $Na^+ = 1$

An elegant example of polymerization involving the formation of μ-oxo bridges has recently been demonstrated by Herrmann et al. (10). Figure 3 shows a simplified reaction scheme for the spontaneous "self assembly" of methyltrioxorhenium monomers to form a three dimensional polymeric rhenium complex. This complex is reported to

have a metallic sheen similar to graphite and exhibits electrical conductivity in the solid state.

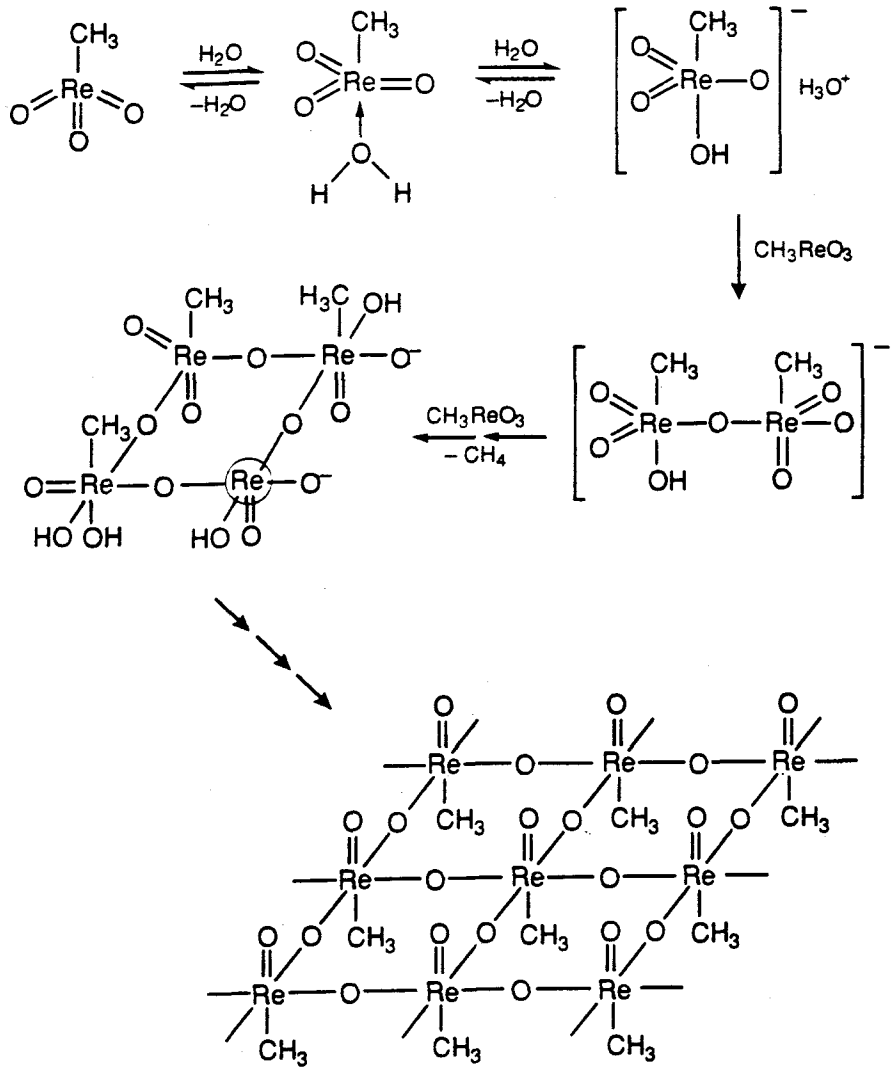

Figure 3. Hydrolysis and polymerization of methyltrioxorhenium (10).

Statement of Objectives

Hydrolysis of 2nd and 3rd Row Platinum Group Metals

The work presented here grew out of the observation that when Pt(II) is coordinated by certain sulfoxide or phosphane ligands, hydrolysis and deprotonation of the aqua ligands results in the formation of di-μ-hydroxo-bisplatinum(II) species, even under strongly acidic conditions (11, 12, 13). We have been interested in exploiting the marked tendency of these Pt(II) complexes to polymerize in acidic solution to develop methods for the systematic preparation of polymeric Pt(II) complexes and the oxidized Pt(IV) counterparts. The following therefore represents fundamental research into the formation of hydroxo bridged complexes and their equilibrium distribution as a function of pH. Of particular importance was determining the driving force behind these reactions, whether they were simply a result of the low pK_a's of the coordinated waters in the monomeric hydrolysis products or whether there was some inherently greater thermodynamic stability conferred on the dimer as compared with the monomer. This last property is reflected in the values of the formation (K_f) and dissociation (K_d) constants shown in Figure 4 below.

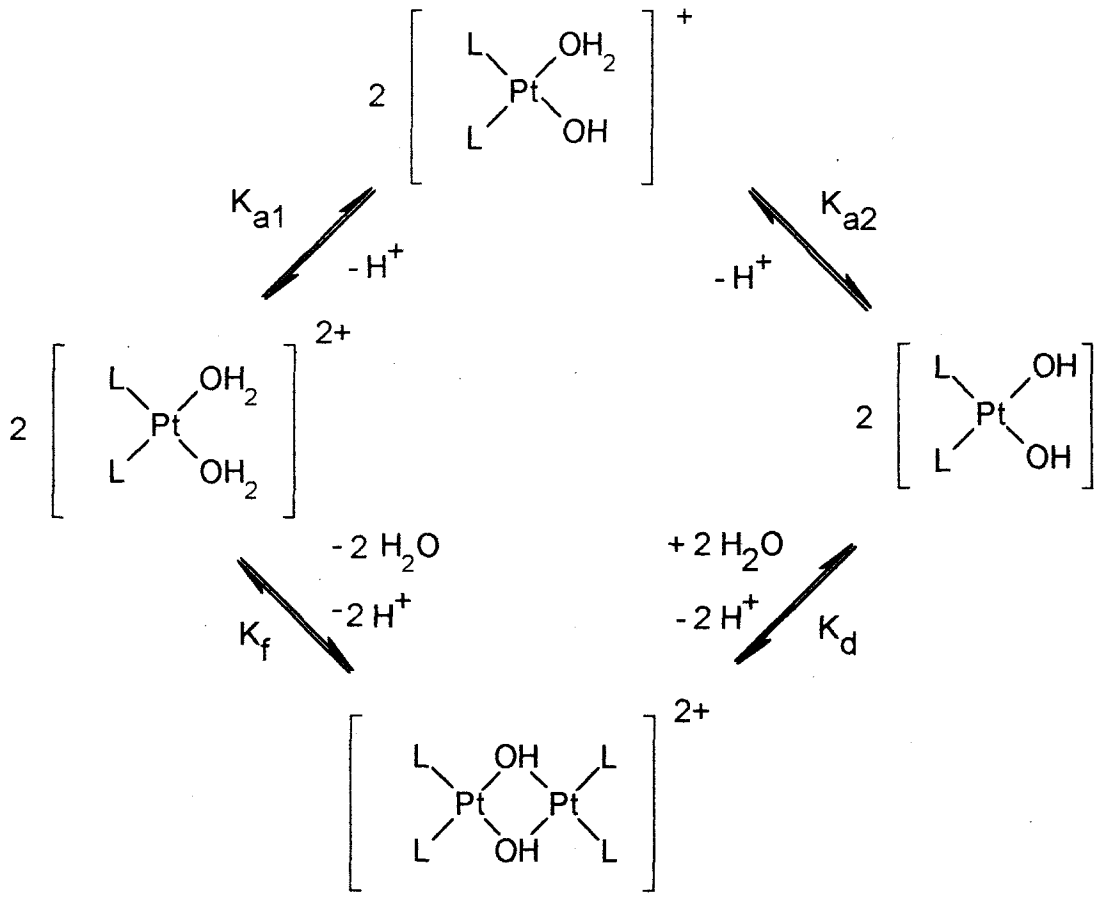

Figure 4. Relationship between K_f, K_d, K_{a1} and K_{a2} for dihydroxo bridged dimers.

As can be seen, the net reaction, starting with the *cis*-diaqua complex, releases two equivalents of water and two protons. Although the detailed mechanism is uncertain, the first step is thought to involve the deprotonation of one of the coordinated waters to form the aqua hydroxo complex. This singly charged cationic

species now has one highly nucleophilic ligand in hydroxide ion and one weakly nucleophilic leaving group in water. Dimer formation then simply requires two of these fragments to come together in the proper orientation, followed by release of the remaining water ligands. Other studies done on similar systems also provide strong evidence to suggest that the mono-deprotonated monomer is the reactive species in dimer formation at near neutral pH (15). At lower pH however, mechanistic studies indicate that the diaqua monomer also makes a substantial contribution to dimer formation (16). Any proposed mechanism for the formation of these dimeric species should be consistent with the established mechanisms for other square planar coordination complexes which normally involves the formation of a five coordinate intermediate (17).

It is useful to compare the mechanism for dimer formation in these four coordinate species with the fairly well established mechanism for hydroxo bridge formation in octahedral six coordinate complexes of other platinum group metals. These systems lend themselves to studies of this kind due in part to the much slower reaction times, with half-lives for the hydrolysis of dibridged Ir(III) amine and ammine complexes ranging from 60 to 9 x 10^6 seconds (18). Figure 5 shows the proposed reaction scheme for the equilibrium between mono- and dinuclear M(III) species (19). These reactions are thought to involve a well defined monohydroxo bridged intermediate shown in the figure. It has been postulated that a major stabilizing influence can be conferred on this intermediate by the hydrogen bonding interaction

shown between the singly coordinated water and hydroxo group of the aqua-hydroxo species.

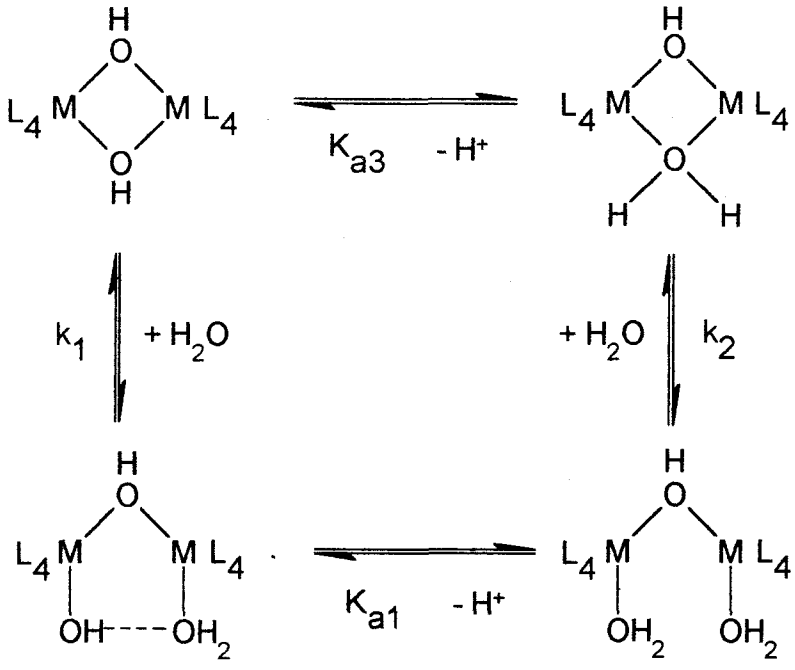

Figure 5. Reaction scheme for the equilibria between dinuclear mono- and dihydroxo-bridged species of Cr(II), Rh(III) and Ir(III). The dashed line indicates a hydrogen bonding interaction. (After Ref. 19)

The existence of this interaction has been confirmed in the solid state by X-ray diffraction data of the Ir(en) complex and is demonstrated in solution by examining the acid strength of mono- and dinuclear species (20). Mono-hydroxo bridged species of sufficient lifetime to be observed by NMR methods have also been postulated for several Pt(II) amine systems (21, 22, 23). Because the nonbonded distances between

the aqua and hydroxo ligands should be comparable in four coordinate square planar and six coordinate octahedral geometries, it is reasonable to expect that the same sort of stabilizing interaction may exist in square planar Pt(II) complexes.

Because these reactions are inherently pH dependent, the majority of our work was restricted to species which were at least partially water soluble. Many sulfoxide and several trialkylphophane ligands form water soluble ionic complexes when coordinated to platinum and were therefore well suited to these investigations. Platinum was additionally convenient for this study due its favorable magnetic properties and intermediate reaction rates.

Practical Applications of the Research

Although the work presented here has concentrated on the basic synthesis and spectroscopic characterization of di-μ-hydroxo bridged complexes, fundamental research into polymerization reactions of this type are important for several reasons. The following briefly examines some of the possible practical applications of this work by discussing several synthetic strategies in which complex structures with very specific chemical and physical properties are "assembled" from two or more smaller fragments.

The systematic design and synthesis of "molecules with function" has recently emerged as an efficient route for more advanced materials applications involving transition metals.

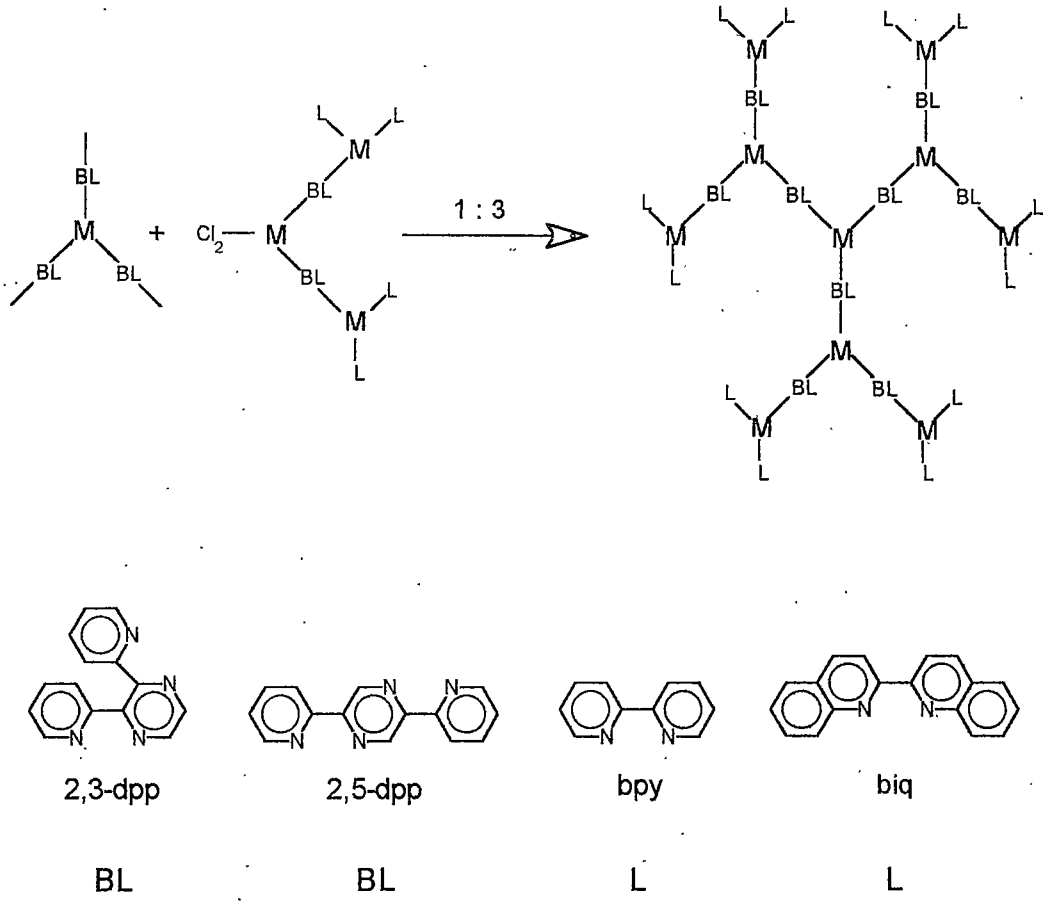

Figure 6: Schematic Diagram of the Structure Directed Synthesis of a High Nuclearity Metal Complex Using Complexes as Both "Metal" and "Ligand" (M = Ru or Os). The bridging (BL) and terminal (L) ligands used are also shown (24).

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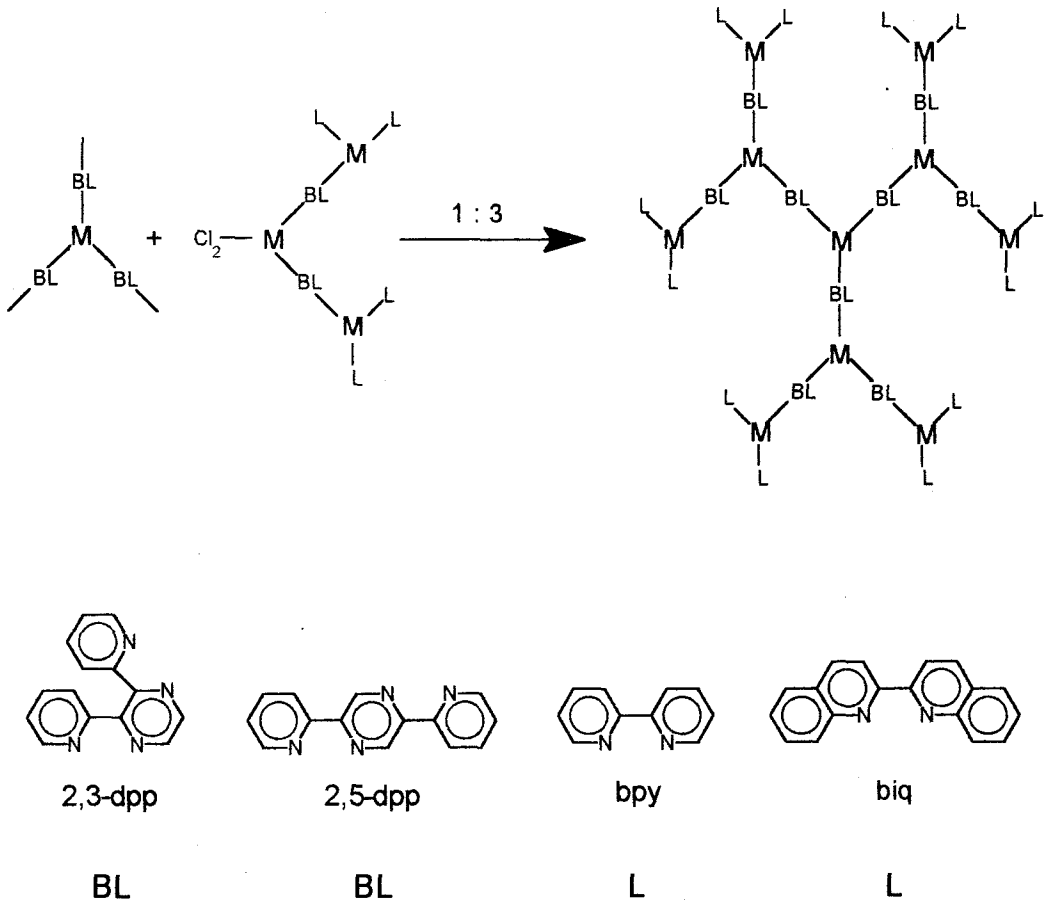
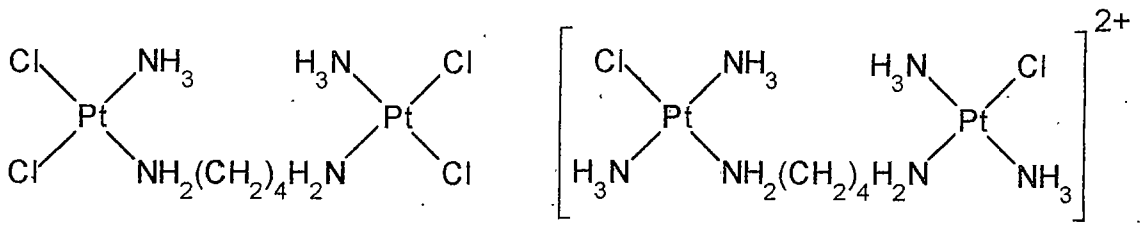


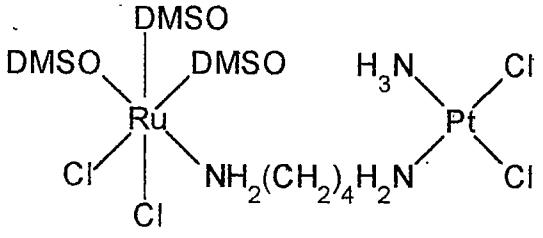
Figure 6: Schematic Diagram of the Structure Directed Synthesis of a High Nuclearity Metal Complex Using Complexes as Both "Metal" and "Ligand" (M = Ru or Os). The bridging (BL) and terminal (L) ligands used are also shown (24).

This strategy makes extensive use of multinuclear complexes as both "metal" and "ligand" and is exemplified by the synthesis of a host of closely related ruthenium complexes which can be systematically designed to possess a wide range of redox and luminescence properties (24). An example of this so called "structure directed synthesis" is shown in Figure 6. In the example shown, chloride provides a labile ligand on the metal atom. If this ligand is hydrolyzed by the addition of a silver salt, a free coordination site exists which is available to the "ligand" complexes. Only a few examples of this approach have been reported for platinum, including the homo- and heterodimeric complexes shown in Figure 7 (25). In this case, the synthesis of these complexes is accomplished by reacting a "precursor" Pt complex with a potentially bidentate amine ligand followed by reaction of the free functionality with a target complex (25). The potential of these complexes as potent second generation anti-tumor agents is discussed below.

A final example of the use of the structure directed approach applied to platinum group metals is seen in the elegant synthesis of bi- and tri-metallic complexes with the potential for applications in molecular circuitry. Figure 8 shows the synthetic use of alkynyl-bipyridine derivatives of Pt(II) as substrates for the addition of ruthenium and/or osmium fragments, resulting in a polymetallic species which shows unique electrical and luminescence properties (26). A brief discussion of molecular wires in the context of partially oxidized and mixed valence platinum complexes is given below.



(Pt, Pt)-2,2 (Pt, Pt)-1,1



(Ru, Pt)

Figure 7. Bimetallic bridged structures formed by reaction of "precursor" and "target" complexes (25).

These examples serve to illustrate the tremendous potential of using polynuclear transition metal species as building blocks for structures with unique physical and chemical properties. It was one of the major goals of this research to determine whether di-μ-hydroxo bridged Pt complexes, with their inherent propensity toward polymer formation, and the availability of two free coordination sites at low pH, could be used in a similar fashion.

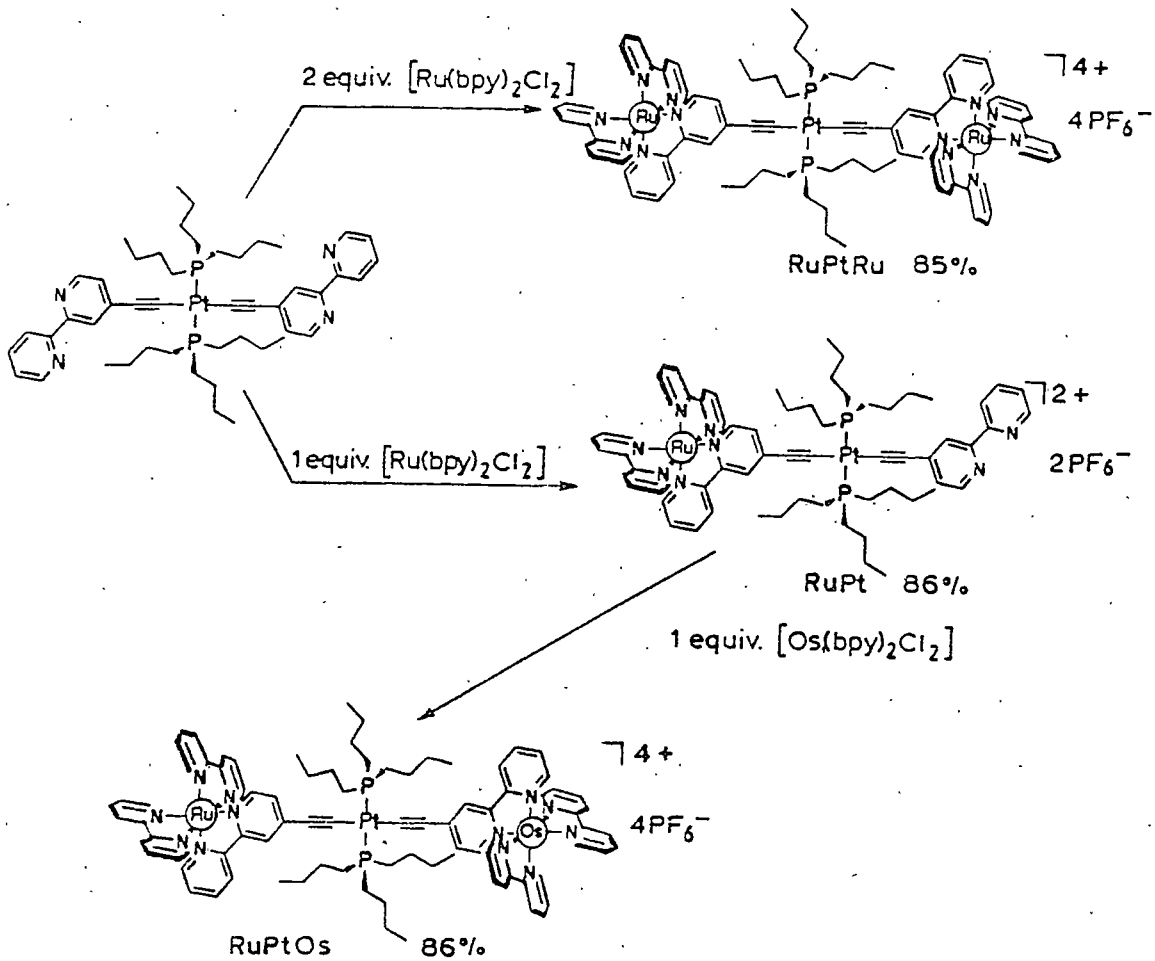


Figure 8. General reaction scheme for the formation of high nuclearity polymetallic complexes (26).

Partially Oxidized and Mixed Valence Complexes

The chemical properties of a transition metal complex can be dramatically altered by oxidation of the metal center. Until recently, the chemistry of platinum has been dominated by the two most stable oxidation states, +2 and +4. Platinum(II) almost invariably forms four coordinate square planar complexes typical of the other d^8

metals including Rh(I), Ir(I), Pd(II) and Au(III) (6). A few five coordinate Pt(II) species are known, including a proposed tri-μ-hydroxobridged dimer (27). These five coordinate species are of interest because of the structural information they may provide concerning the transition states for associative substitution reactions of square planar complexes. As mentioned previously, these reactions normally proceed through five coordinate trigonal bipyramidal intermediates (17). For first row d^8 metals such as Ni(II), tetrahedral complexes are formed with the weaker field ligands such as chloride and bromide, whereas square planar complexes are formed with strong field π donor ligands such as CN^- (28). The square planar configuration is favored over tetrahedral or octahedral geometry in this case due to the increased ligand field stabilization energy. This behavior can be explained using simple crystal field theory by appealing to the energy level diagram shown if Figure 9.

This diagram shows the ligand field splitting for tetrahedral, octahedral and square planar d^8 complexes as well as the tetragonal distortion representing the transition from octahedral to square planar geometry (29). In this diagram, the overall energy of the system can be lowered by pairing electrons in the d_{xy} orbital as the geometry moves from octahedral to square planar.

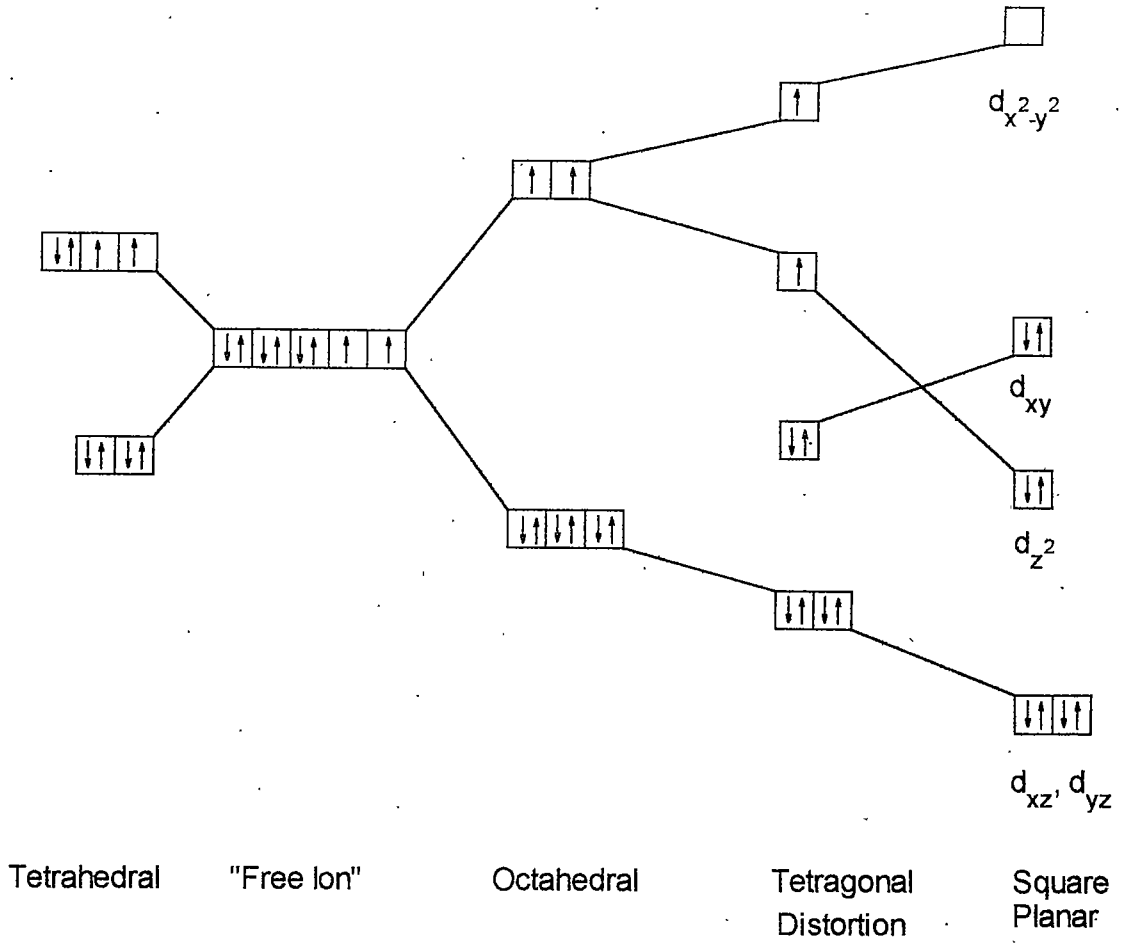


Figure 9. Ligand field splitting for hypothetical tetrahedral, octahedral and square planar d^8 coordination geometries (After Ref. 29).

Oxidation of Pt(II) to Pt(IV). Oxidation to the substitutionally inert Pt(IV) state can be accomplished by a variety of oxidizing agents. For the dimeric complexes being considered here, formation of the Pt(II) species followed by oxidation of one or both of the metal atoms could serve to lock the ligands in place, and would represent a significant step in being able to manipulate the reactivity of the dimer fragment. Only

one example of this type of reaction has been reported in the literature (30) (Figure 10). Hydrogen peroxide has also been shown to be effective at oxidizing *bis*-oxalato Pt(II) to the Pt(IV) *trans* dihydroxo complex. The mechanism for that reaction has been determined by ^{195}Pt NMR studies using isotopically labeled H_2O (31).

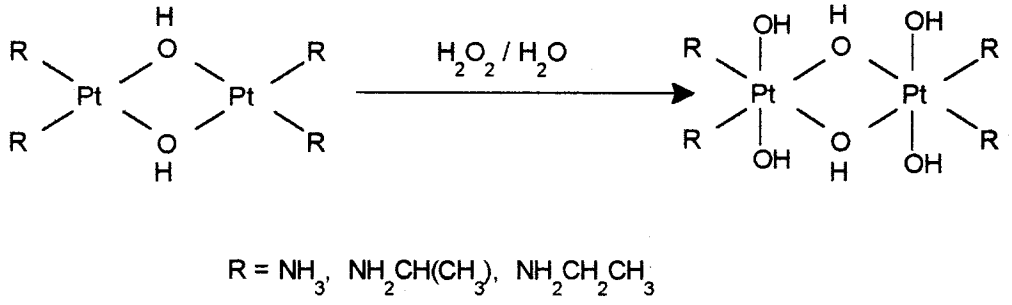
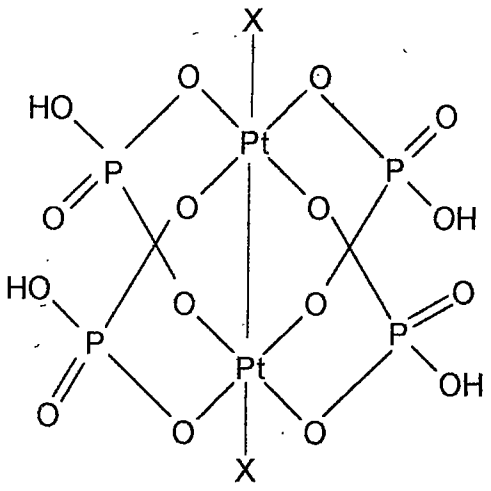


Figure 10. Oxidation of Pt(II) dimer with hydrogen peroxide (30).

Other oxidizing agents have also been successfully utilized for the oxidation of Pt(II) species, including cerium (IV), chlorine, bromine, monopersulfate ion and Pt(IV) (32, 33, 34, 35). Two electron oxidation with halogens normally produces the corresponding *trans* dihalo Pt(IV) species but also may result in halogen substitution on the more labile Pt(II) species if the reaction is carried out in aqueous solution. Because molecular chlorine disproportionates in aqueous solution, parallel oxidation by Cl_2, HOCl, and OCl^- always occurs, the relative importance of each species being a

function of pH and concentration of free chloride. Details of reactions involving oxidation of monomeric and dimeric Pt(II) complexes pertinent to this investigation are discussed more fully in the Results and Discussion Section below.

The intermediate oxidation state of Pt(III) plays an important role in the formation of metal-metal bonded complexes and partially oxidized linear chain conductors. These octahedral d^7 complexes are substitutionally labile as well as being paramgnetic due to the unpaired electrons in the d_{xy} orbital. One of the most intensively studied classes of dimeric Pt(III) species is exemplified by the bridged pyrophosphito complex shown in Figure 11. In this structure, the metal p_z-p_z and d_z^2-d_z^2 orbitals interact along the Pt-Pt axis to form a single metal-metal bond (36). A very important fundamental difference exists between the bridging geometry of this complex and the di-μ–hydroxo bridges discussed in this thesis. In the case of $[Pt_2(\mu\text{–}PO_4H)_4]^{2-}$ the three atom span and the tetrahedral geometry around the interdonor oxygen atom create a face to face orientation of the PtO_4 units, thereby allowing the d_z^2 orbitals on each platinum atom to interact. Bonded Pt-Pt distances in these diplatinum (III,III) complexes range from 2.716 Å to 2.760 Å depending on the axial ligand, X (2). This range can be compared with the non-bonded Pt--Pt distance in di-μ–hydroxo bridged complexes which are all greater than 3 Å.



$X = CN^-, NO_2^-, NH_3$

Figure 11. Pyrophospito bridged Pt(III) dimer (36).

It remains to be seen whether Pt-Pt bonds can be induced to form upon one electron oxidation of these dimeric species. The oxidation of mono- and dimeric Pt(II) sulfoxide and phosphane complexes is discussed more fully in the Results and Discussion section.

Although the individual d^7 metal centers are paramagnetic due to a single unpaired electron, polymer formation results in an overall diamagnetic "d^{14}"complex which can be studied by nuclear magnetic resonance spectroscopy. Chemical shifts have been reported for these complexes and appear to lie roughly midway between the