PART I: COORDINATION CHEMISTRY OF HIGH-VALENT OSMIUM POLYANIONIC CHELATING LIGAND COMPLEXES WITH IMINE, IMIDO AND NITRIDO LIGANDS

PART II: ASYMMETRIC HYDROGENATION USING A RESOLVED CHIRAL SCANDIUM HYDRIDE COMPLEX

Thesis by

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To My Dad,

Who never thought he'd live to see this day, and sadly, didn't.

And To My Mom,

Who never gave up on me.

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Abstracts

Part I: The chemistry of high-valent osmium polyanionic chelating ligand complexes with imine, imido and nitrido ligands is explored. The synthesis and x-ray diffraction study of Os(η^4-HBA-B)($NC_6H_5NHC_6H_4$) is reported. A neutral, octahedral Os(VIII) intermediate complex is postulated. The synthesis and x-ray diffraction study of [OsN(η^4-HBA-B)]$^-$ is reported. The mechanism of formation is discussed. These complexes represent two of the first examples of non-planar amide ligands in transition metal chemistry. The synthesis of a five-coordinate imido complex, Os(N-$C_{10}H_{16}$), is reported. The formation of the first osmium-osmium quadruply-bonded complex, [Os(η^4-HBA-B)]$_2$, is reported. Reactions with the nitrido complex, [OsN(η^4-HBA-B)]$^-$, and the methylimido complex, OsNMe(η^4-HBA-B), are also reported.

Part II: The asymmetric hydrogenation of the prochiral substrate, methylene indane, is induced by the resolved chiral scandium complex, $Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-(C_5H_3(1R,2R,5S)-menthyl)ScH, in substoichiometric quantities. Methylene indane is hydrogenated to produce methylindane with an enantiomeric excess of 34% and a maximum turnover of four.

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PART I: COORDINATION CHEMISTRY OF HIGH-VALENT OSMIUM POLYANIONIC CHELATING LIGAND COMPLEXES WITH IMINE, IMIDO AND NITRIDO LIGANDS

CHAPTER ONE: INTRODUCTION TO OXIDATION CHEMISTRY AND LIGAND DESIGN

Oxidation chemistry is currently an important area of research because of its main role in many industrial processes, including such applications as the Wacker process in which ethylene is oxidized to acetaldehyde[1], the Mid-Century process[2] for the production of terephthalic acid and the Oxirane process[3] for the epoxidation of olefins, among others. In addition, oxidation of hydrocarbons from petroleum feedstocks is an important area of research in the production of commodity chemicals and fuels.[4] Oxidative processes also play a role in drug design and in many biological systems.[5] Different approaches have been taken towards developing more efficient oxidizing capabilities such as enzymatic oxidations[6], reactions with molecular oxygen[7], the use of non-metal oxidants such as peroxides[8] and oxidizing transition metal complexes.[9] Even though metals, and in particular, transition metals, play a crucial role in oxidation chemistry, this area has received relatively little attention from the inorganic research community. The chemistry of low-valent transition metals is much more developed than the chemistry of high-valent complexes.

The main goals of oxidation chemistry are to produce better oxidizing agents that perform selective transformations, characterize completely the active oxidizing agent and elucidate the operative mechanisms behind these reactions. Associated with these objectives are several critical problems. Catalytic oxidation processes tend to rely on metal-based heterogeneous systems which are extremely hard to study, and the catalysts tend to be poorly characterized.[10] In addition, most of the oxidation catalysts employed are not selective. It is frequently difficult to control the oxidation resulting in either over-oxidation of the substrate or a mixture of products which then have to be separated. These kinds of problems are perfectly illustrated in the oxidations using Cr(VI) and Mn(VII) as the oxidants that are among the most common reagents employed in organic chemistry.[11,12] The major source of the non-selectivity is that the metals perform the first oxidation and are then themselves reduced, but the reduced metal species can *also* act as an oxidation catalyst. Oxidations with Cr(VI) and Mn(VII) yield an overall reduction of three- or four-electrons at the metal center, whereas an organic substrate is

usually oxidized by only two electrons. Ultimately, a chain of oxidations occurs with a number of oxidized products resulting, as illustrated in Equation 1.1.

(1.1)

$$(CH_3)_2CHOH + Cr(VI) \longrightarrow (CH_3)_2C{=}O + Cr(IV)$$

$$(CH_3)_2CHOH + 2Cr(IV) \longrightarrow 2(CH_3)_2\dot{C}OH + 2Cr(III) + 2H^+$$

$$2(CH_3)_2\dot{C}OH + 2Cr(VI) \longrightarrow 2(CH_3)_2C{=}O + 2Cr(V) + 2H^+$$

$$2Cr(V) \longrightarrow Cr(IV) + Cr(VI)$$

$$3(CH_3)_2CHOH + 2Cr(VI) \longrightarrow 3(CH_3)_2C{=}O + 2Cr(III) + 6H^+$$

Although this particular reaction is selective for the conversion of isopropanol to acetone, any other substrate produces a mixture of products.[11]

The Collins group believes that one of the main reasons for the lack of selective, well-characterized oxidizing agents is the limited nature of ligands available that will stabilize transition metals in high oxidation states. The scope of ligands capable of stabilizing high oxidation state metal complexes has traditionally been limited to oxo, nitrido and halide ligands.[13] More recently, ligands such as porphyrins[14] and salen-type[15] ligands have been developed.[11] While work in these areas is important, it is necessary to develop new types of ligands that can stabilize high oxidation state metal complexes, designed to undergo only two-electron reductions and serve as selective oxidizing agents.

The Collins group approaches this problem by designing and synthesizing Polyanionic Chelating (PAC) ligands that will allow the development of high oxidation state inorganic complexes for use as oxidizing agents. A major goal has been to establish the design criteria for the kinds of ligands that would be compatible with high oxidation state chemistry. The necessary features include: (1) resistance to oxidation; (2) the formation of five- and six-membered metallacycles upon coordination; (3) negative charge sufficient to counter the positive charge of the metal center; (4) chemically innocent binding sites that are resistant to hydrolysis and other displacement reactions; (5) ease of derivatization to vary the oxidizing

power of the complex and to incorporate steric bulk or chiral centers and; (6) convenient synthesis.

In accordance with these criteria, the design and synthesis of polyanionic chelating (PAC) ligands such as H_4HBA-Et, 1, H_4CHBA-Et, 2, H_4HBA-B, 3, H_4CHBA-DCB, 4, H_4HMPA-B, 5, and H_4HMPA-DMP, 6, have been accomplished (see Figure 1.1). These ligands have been successfully complexed with a variety of metal centers. Complexes of Ni, Cu, Co, Mn, Cr and Os have been fully characterized and a number of interesting reactions have been discovered.[16a-f] The desired mode of bonding to transition metals is shown in Figure 1.2. The ligands coordinate through the fully deprotonated amido and hydroxyl groups as tetraanions and form either five or six-membered chelating rings with the metal center.

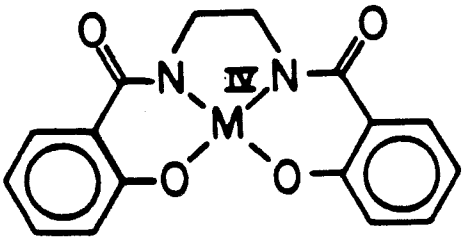
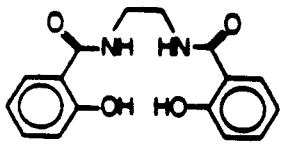


Figure 1.2. The desired mode of coordination of a PAC ligand

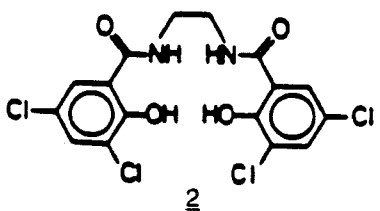
One of the first PAC ligands to be synthesized was 2. After an extensive investigation, it was discovered that the ethylene bridge is susceptible to oxidation and participates in a cascade of degradation processes. One of the metal species was found to be a catalyst for the electrochemical oxidation of alcohols.[17] A scheme showing the remarkable degradation of this ligand is illustrated in Scheme 1.1.

Because the ethylene bridge is susceptible to oxidation, a new set of ligands, 3 and 4, were designed to eliminate this possibility by replacing the ethylene backbone with a phenylene bridge. These new ligands provided a wealth of reactions (see Scheme 1.2) when coordinated



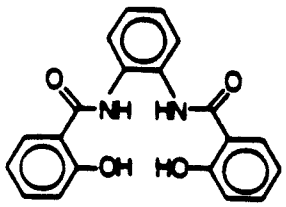
1

H_4HBA-Et



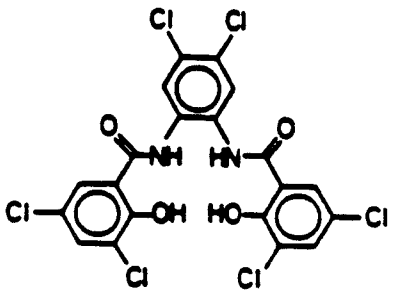
2

H_4CHBA-Et



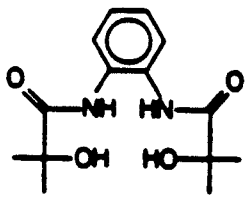
3

H_4HBA-B



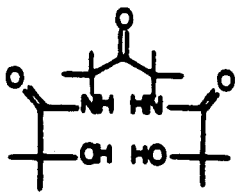
4

H_4CHBA-DCB



5

H_4HMPA-B



6

H_4HMPA-DMP

H_4HBA-Et ≡ 1,2-bis(2-hydroxybenzamido)ethane

H_4CHBA-Et ≡ 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane

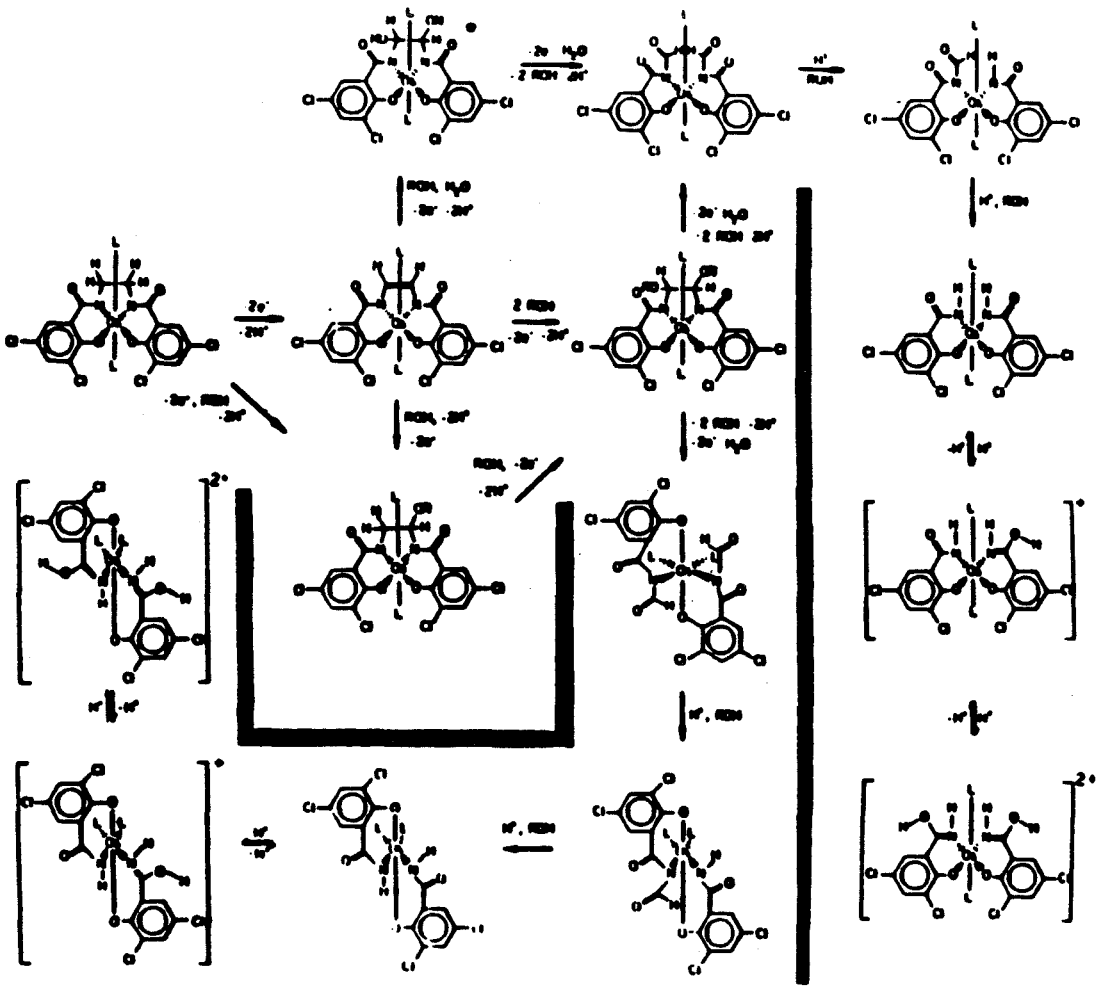
H_4HBA-B ≡ 1,2-bis(2-hydroxybenzamido)benzene

H_4CHBA-DCB ≡ 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene

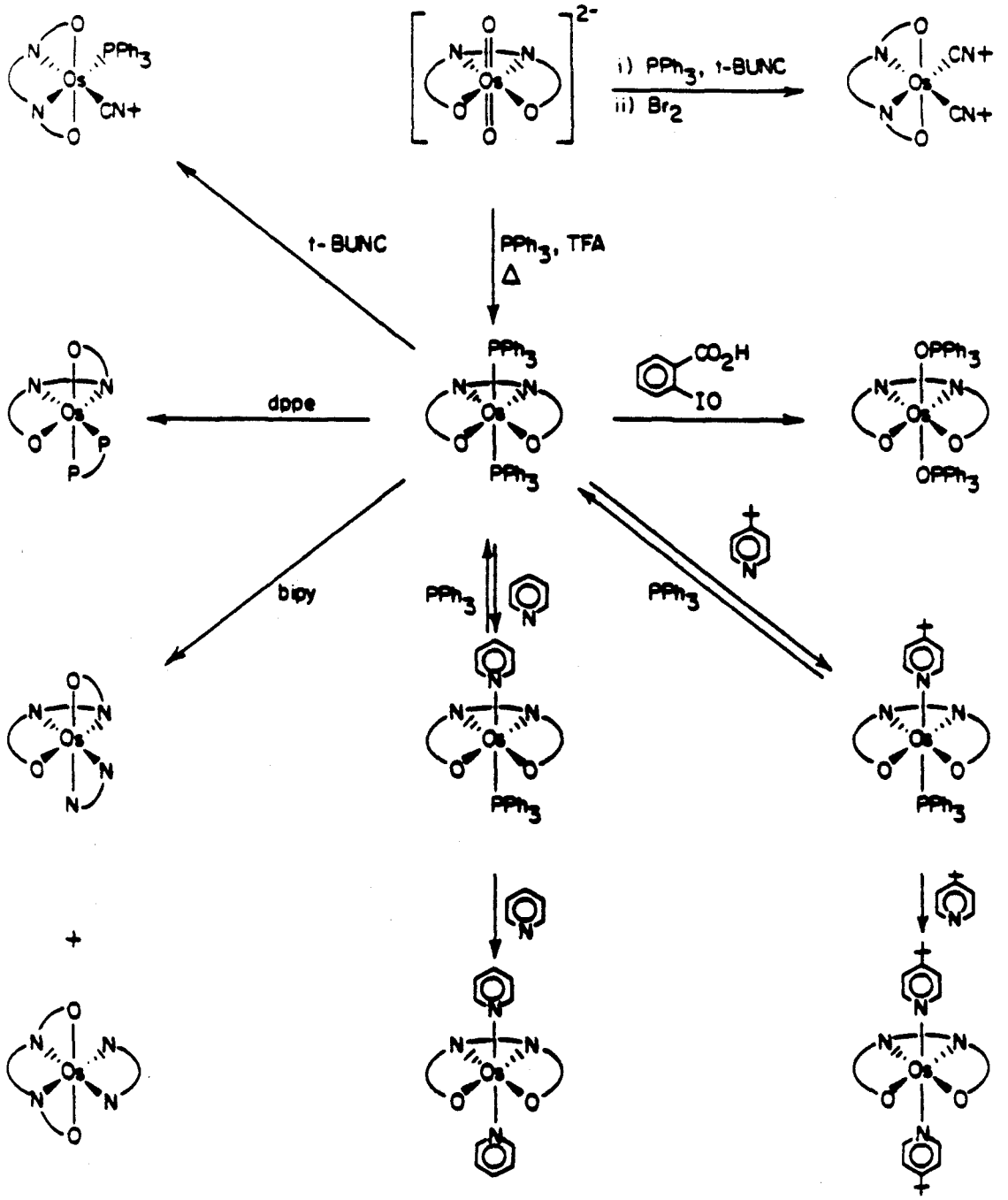
H_4HMPA-B ≡ 1,2-bis(2-hydroxy-2-methylpropanamido)benzene

H_4HMPA-DMP ≡ 2,4-bis(2-hydroxy-2-methylpropanamido)-2,4-dimethylpentan-3-one

Figure 1.1. Commonly used polyanionic chelating (PAC) ligands.



Scheme 1.1. Oxidative and hydrolytic decomposition of *trans*-Os(η^4-CHBA-Et)(py)$_2$.



Scheme 1.2. Synthesis of Os(IV) complexes.

to osmium and led to the discovery of three isomers for octahedral PAC ligand complexes and the suspicion that the ligands are not as innocent as was first hoped.

The PAC ligands 3 and 4 can exist in three geometries labeled *cis-α*, *cis-β* and *trans*, as depicted in Figure 1.3.[18]

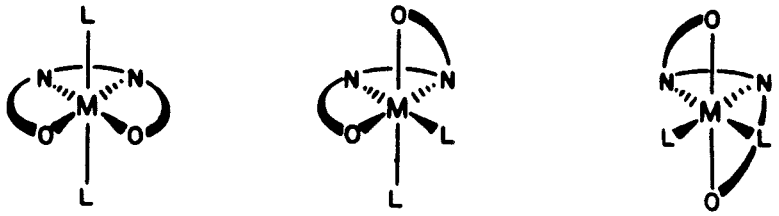
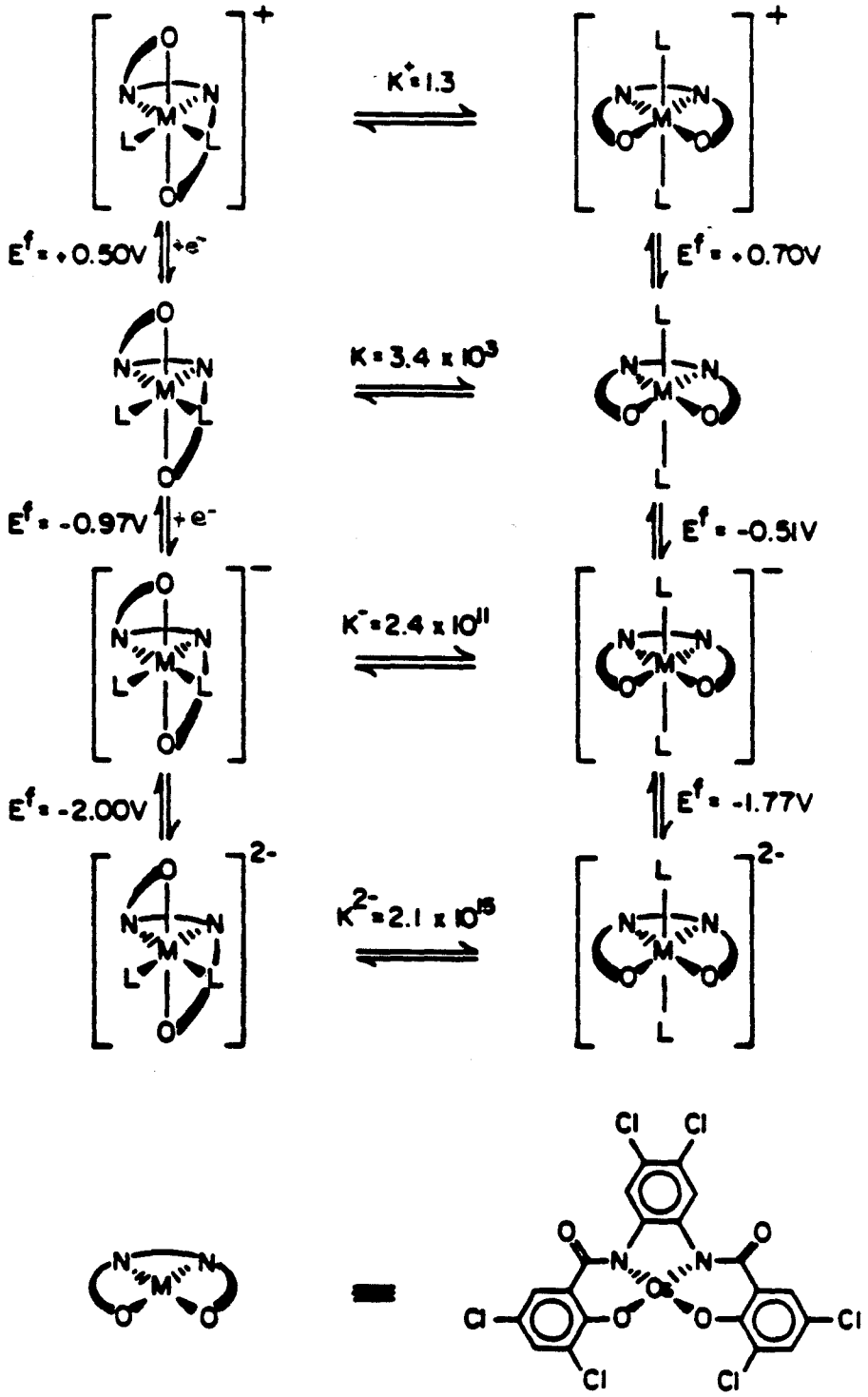


Figure 1.3. Nomenclature for the three possible isomers of a PAC ligand.

Three reasons for these isomerizations have been discovered: The ligand rearranges in response to the electronic requirements of the metal center as a result of structural constraints imposed by the other ligands, and in response to steric repulsion. A detailed study of the thermodynamic relationship among these isomers was made (see Scheme 1.3).[19] These isomerizations led to the discovery that in the *cis-α* and *cis-β* forms the amide groups are non-planar. PAC ligand complexes are the first examples of non-planar amide ligands in coordination chemistry.[18] During the course of these studies, however, it also became clear that the PAC ligands 3 and 4 were capable of resonance forms that would reduce the oxidation state at the metal center,as shown in Figure 1.4.[18]



Scheme 1.3. Thermodynamic relationships between *cis* and *trans* isomers in different oxidation states.

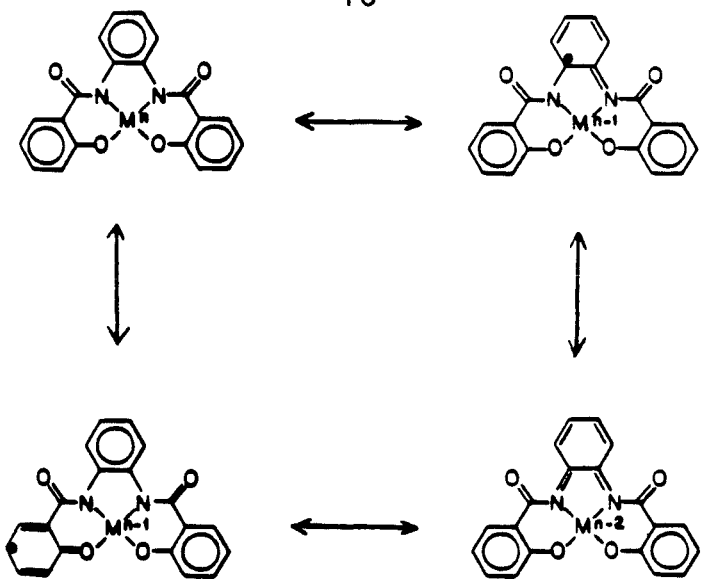
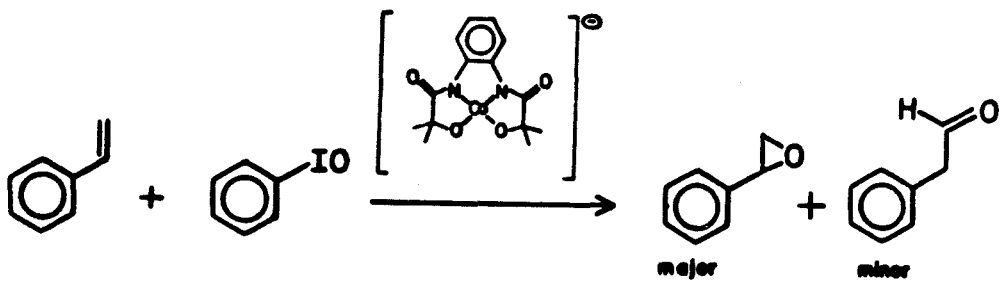


Figure 1.4. Resonance structures of a coordinated PAC ligand.

To eliminate the non-innocence of the PAC ligands 3 and 4, the PAC ligands were redesigned again, and the aromatic ligand "arms" were replaced by an aliphatic bridge between the hydroxyl group and the amide carbonyl. The final PAC ligands, 5 and 6 fulfill all of the criteria outlined above. Cobalt complexes of 5 were found to catalyze the epoxidation of olefins such as styrene (see Equation 1.2).[16c] Studies with these new ligands are ongoing.

(1.2)



The work reported in Part One of this thesis is part of the larger work of the Collins group. The overall major goals are to synthesize and explore the chemistry and oxidizing abilities of new high oxidation state transition metal complexes using rationally designed PAC

ligands. The specific goals of the research reported here are to prepare high oxidation state complexes containing unsaturated nitrogen ligands and determine whether or not oxidizing capabilities exist.

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PART ONE: COORDINATION CHEMISTRY OF HIGH-VALENT OSMIUM POLYANIONIC CHELATING LIGAND COMPLEXES WITH IMINE, IMIDO AND NITRIDO LIGANDS

CHAPTER TWO: SECTION I– REACTIONS OF Os(η^4-HBA-B)(PPh_3)$_2$ TO FORM IMINE, IMIDO AND NITRIDO LIGAND COMPLEXES

Introduction and Background

There has been a great deal of interest recently in multiply-bonded ligand complexes; for example, carbene (CR_2)[1] and carbyne (CR)[1] complexes have been the focus of intensive research efforts. Transition metal oxo ("oxene" (O) complexes are widely used in oxidation chemistry and research continues in this area.[2] Less attention has been directed to imido ("nitrene") (NR)[1,3] and nitrido ("nitryne") (N)[1,4] complexes.

Imido ligands are isoelectronic with the oxo ligand and like the oxo ligand, exhibit strong π-bonding to metals, making these ligands particularly well suited for high oxidation state chemistry. An interesting feature of the oxo and imido ligands is the possibility of forming a triple bond to the metal for which the bonding modes are illustrated in Figure 2.1.

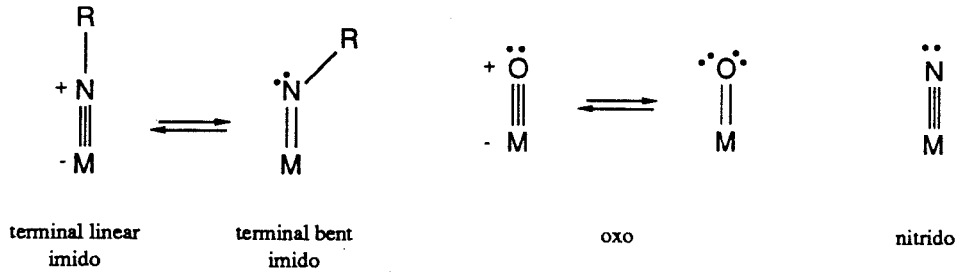


Figure 2.1. Bonding modes for oxo, imido and nitrido ligands.

The terminal linear bonding mode for the imido moiety is the one most commonly observed in crystal structures. The terminal bent mode can be expected only when a linear bonding mode causes the electron count to exceed the eighteen-electron rule.[3]

Bisimido Project--Introduction

PAC ligands have the ability to form unusual complexes. The efficient donor abilities of the PAC ligands stabilize metal complexes in unusually high oxidation states, and the reaction chemistry available to these novel compounds has not yet been fully explored. The formation and subsequent reaction chemistry of unsaturated metal-nitrogen bonded PAC complexes

should be particularly interesting. The first area of inquiry was centered around the efforts to prepare a neutral Os(VIII) bisimido PAC ligand complex.

In 1956, Kobayashi reported the first imido complex (t-Bu-N)OsO_3.[5] Since then, many imido complexes, most of them with Group IVB and VIIIB metals, have been prepared, which are thermally stable and in many cases air stable. Relatively few bisimido complexes have been reported which is in sharp contrast to the tremendous wealth of their dioxo analogues. Four-coordinate bisimido complexes are known for osmium, chromium, molybdenum, tungsten and platinum.[6] To date, only one octahedral bisimido complex has been characterized.[7] The bonding for a bisimido compound is quite interesting because there cannot be two full triple bonds in a cis structure (utilizing only the metal dπ orbitals); the two amphoteric ligands thus lead to several possible bonding modes shown in Figure 2.2.[7]

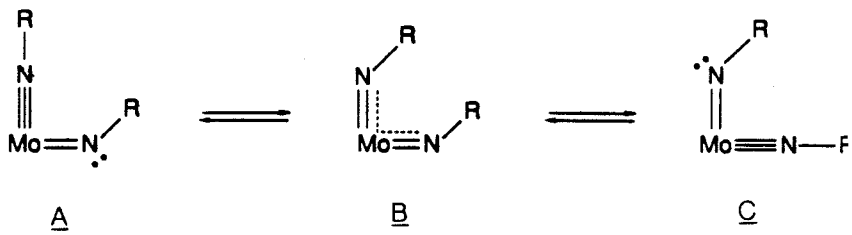


Figure 2.2. Bonding modes for bisimido complexes.

Crystallographic and variable temperature NMR studies are in better accord with the delocalized structure, B.

In addition to the interesting structural questions, there are several other motivations for pursuing the synthesis of bisimido complexes. These considerations, which will be further discussed below, include: (1) an effort to extend the basic reactions available to the PAC ligand complexes and to probe the effects of strong π-donors on PAC ligand isomerization in high oxidation state complexes, (2) preparation and isolation of the first neutral, octahedral Os(VIII) complex, and (3) development of bisimido complexes for use as nitrene (:NR) transfer reagents for organic substrates.

A noteworthy structural feature of the PAC ligands is the ability to isomerize in response to the electronic requirements of the metal (see Chapter One). *Trans*, *cis*-α and *cis*-β diasteriomers of PAC ligand complexes have all been characterized (see Figure 1.3). It has been established by an examination of the electrochemistry of these compounds that the *trans* form is the least donating and the *cis*-α geometry is the most electron-releasing.[8] It would be very interesting to determine the PAC ligand geometry in an octahedral bisimido complex. Although the metal center would be formally d^0 (OsVIII), the imido ligands are among the strongest π-donor ligands known, and the PAC ligand may not be required to isomerize to the most donating (*cis*-α) form. The strength of the imido π-donation may give rise to unusual reactivities as well as to interesting structural features such as the capability of functioning as nitrene transfer reagents.

To date, all of the Os(VIII) compounds known invariably contain O^{-2}, F^- and/or N^{-3} ligands.[9] Isolation and characterization of a bisimido PAC ligand osmium complex would represent the first example of a well-characterized neutral octahedral Os(VIII) compound. Such a compound is of particular interest considering that the Os(VIII) species, OsO_4, is a powerful oxidizing agent used extensively in organic chemistry. It was hoped that the electronic properties of the compound could be tuned by varying the nature of the PAC ligand. This assumption was based on electrochemical data such as are shown in Table 2.1.[8]

(Volts vs. Fc+/Fc)

Compound	III/II	IV/III	"V"/IV
trans-Os(η^4-HBA-B)(PPh_3)$_2$	-1.66	-0.44	+0.71
trans-Os(η^4-CHBA-DCB)(PPh_3)$_2$	-1.72[a]	-0.46	+0.59
trans-$OsCl_4$(PPh_3)$_2$		-0.12	+1.34[a]
$[OsCl_6]^{2-}$		-1.19	+0.74

[a] Couple is irreversible.

Table 2.1. Formal potentials for osmium complexes

The preparation of a neutral Os(VIII) complex with PAC ligands that could be tuned for specific oxidizing abilities was one of the main thrusts in this project.

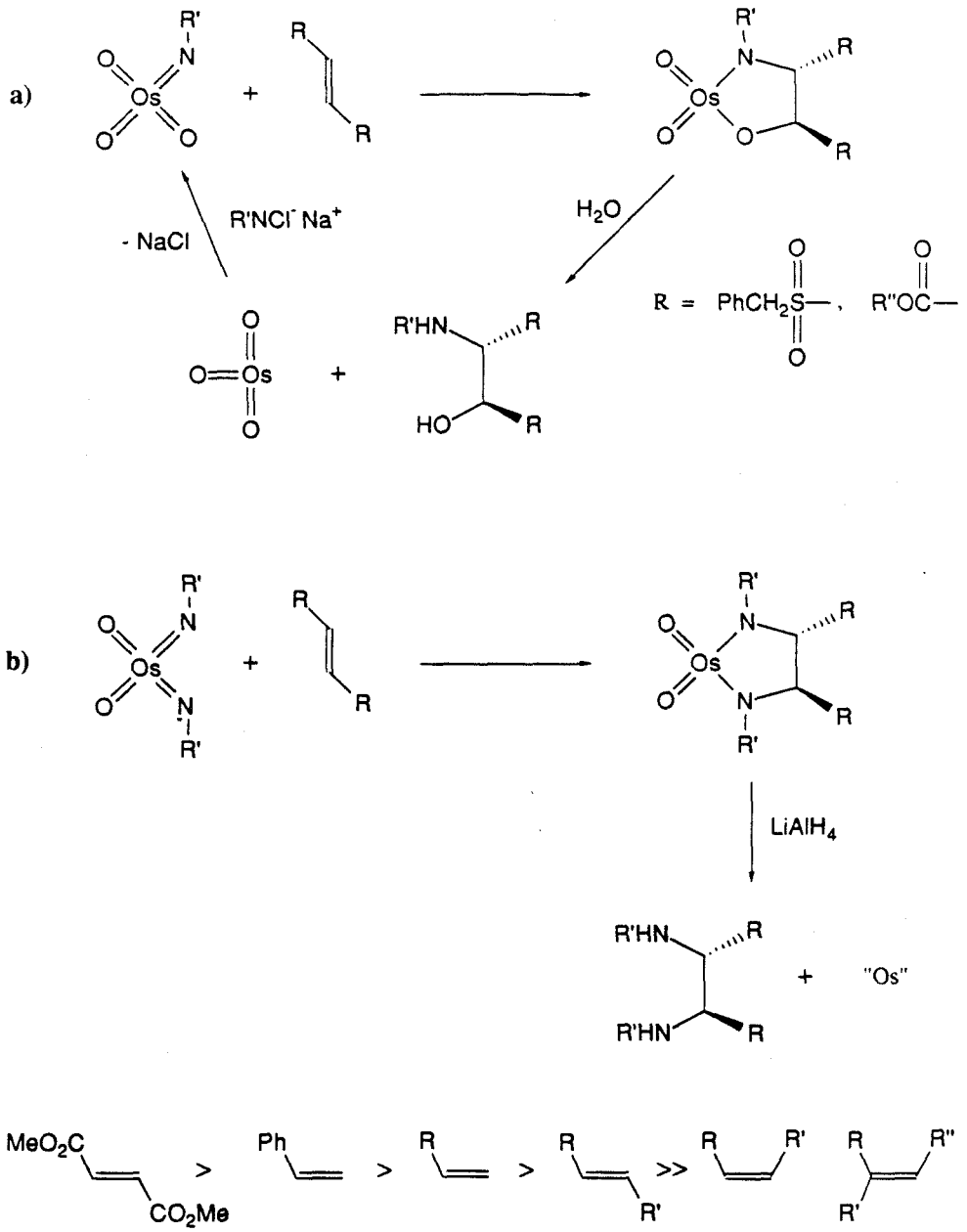
Bisimido complexes can potentially function as a source of nitrene transfer reagents for use in organic synthesis. Metal imido complexes may offer advantages over nitrene fragments generated in organic media which are not always very selective.[10] Although monoimido complexes in general tend to be fairly inert and react only under forcing conditions,[11] Schrock and Nugent have reported metathesis-like reactions for tantalum imido complexes (see Equations 2.1 and 2.2, respectively).[12,13]

(2.1) $Ta(NPh)(THF)_2Cl_3 + PhCHO \longrightarrow PhCH{=}NPh + "TaOCl_3(THF)_2"$

(2.2) $Ta(NR)(NR'_2)_3 + \rangle{=}O \longrightarrow \rangle{=}NR' + "Ta"$

Bisimido complexes, however, are expected to be more reactive.[7] For example, the series $OsO_n(NR)_{4-n}$ (n=2,1) was found by Sharpless and co-workers to be quite reactive towards olefins (see Scheme 2.1).[14] Vicinal oxyaminations and diaminations proceed smoothly in moderate-to-good yields with electron-deficient olefins. Such transformations are potentially very useful to synthetic chemists. Unfortunately, the Sharpless system appears to be limited to electron-poor olefins in the *trans* configuration. With the synthesis of PAC bisimido complexes, it was hoped that the generality of this reaction could be increased and extended to include other substrates such as ketones, dienes, α,β-unsaturated ketones and thioketones.

Many synthetic routes are available to imido complexes. A recent review outlined many of these and the most common syntheses are shown in Table 2.2.[3] The most promising of these synthetic methods appeared to be the organic azide route; this method was explored first.



Scheme 2.1. Oxyamination and diamination reactions.

(a) Deprotonation of primary amines

$$MCl_2RNH_2 \longrightarrow M(NR)$$

$$M{=}O + RNH_2 \longrightarrow M(NI$$

$$M(NR'_2)_2 + RNH_2 \longrightarrow M(I$$

(b) Use of silylamines

$$M{=}O + RN(SiMe_3)_2 \longrightarrow M(NF$$

$$Cl{-}M{=}O + 2RNH(SiMe_3) \longrightarrow$$

$$+ Me_3SiNH_2R^+Cl$$

(c) Alkylation of nitrido complexes

$$M{\equiv}N + RX \longrightarrow M(NR)^+$$

(d) Oxo/imido exchange reactions

$$M{=}O + R_3PNR \longrightarrow M(NR)$$

$$M{=}O + RNCO \longrightarrow M(NR)$$

$$M{=}O + RNSO \longrightarrow M(NR)$$

(e) Addition of chloramine

$$M + RNHCl \xrightarrow{\text{base}} M(NF$$

(f) Oxidation of metal carbonyls

$$M(CO)_2 + RNO_2 \rightarrow M($$

$$M(CO)_2 + RN_3 \longrightarrow$$

(g) Addition of organic azides

$$M + RN_3 \longrightarrow$$

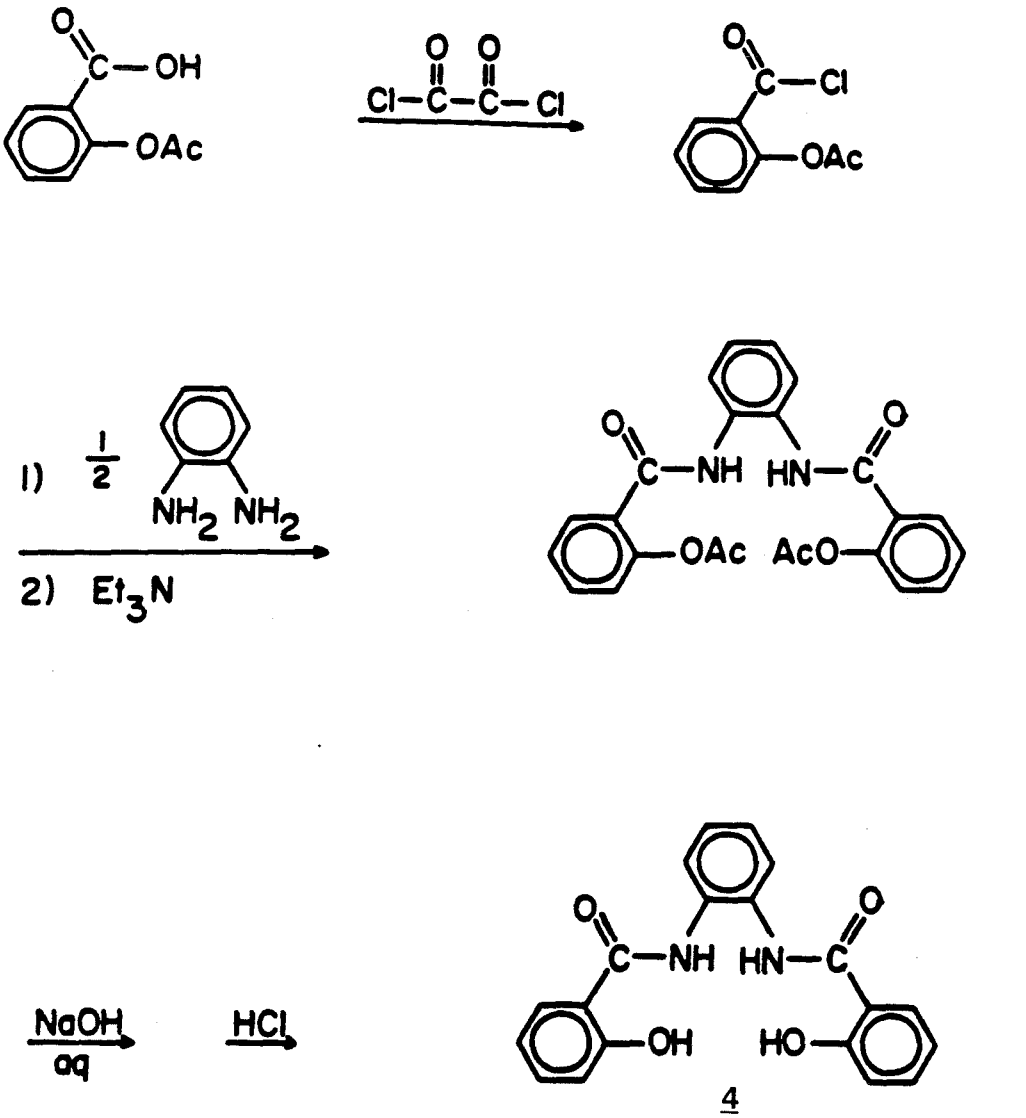
Table 2.2. Convenient syntheses for transition metal imido complexes.

Results and Discussion

As a result of the pioneering work of the Collins group in preparing unusual PAC ligand complexes in high oxidation states, a number of high-valent complexes are available for reactivity studies. The chemistry of the osmium complexes is the most developed, largely because the higher oxidation state osmium complexes still exhibit useful ^{1}H NMR spectra, despite their paramagnetism, which greatly aids in characterization. For these reasons, the osmium complexes were selected to carry out studies involving unsaturated nitrogen ligands.

Most of the coordination chemistry with unsaturated nitrogen ligands was explored using a single PAC ligand, (η^4-HBA-B), 4,. This ligand was chosen because it is easily synthesized and allows easy access to many readily synthesized starting material complexes. The synthesis of 4 is straightforward and is shown in Scheme 2.2. 4 can be complexed to osmium according to Scheme 2.3. Reduction of the dioxo, Os(VI) complex, [K_2][Os(η_4-HBA-B)(O)$_2$], 7, with PPh_3 leads to the neutral Os(IV) complex, Os(η^4-HBA-B)(PPh_3)$_2$, 8 (see Scheme 2.3). One of the phosphine ligands is quite labile and can be readily displaced, allowing coordination of a variety of ligands. Both phosphine ligands can sometimes be replaced under more severe conditions or by dichelating ligands. Much of this chemistry has been reported elsewhere.[8] Here developments of the chemistry of 8 with unsaturated nitrogen ligands is reported.

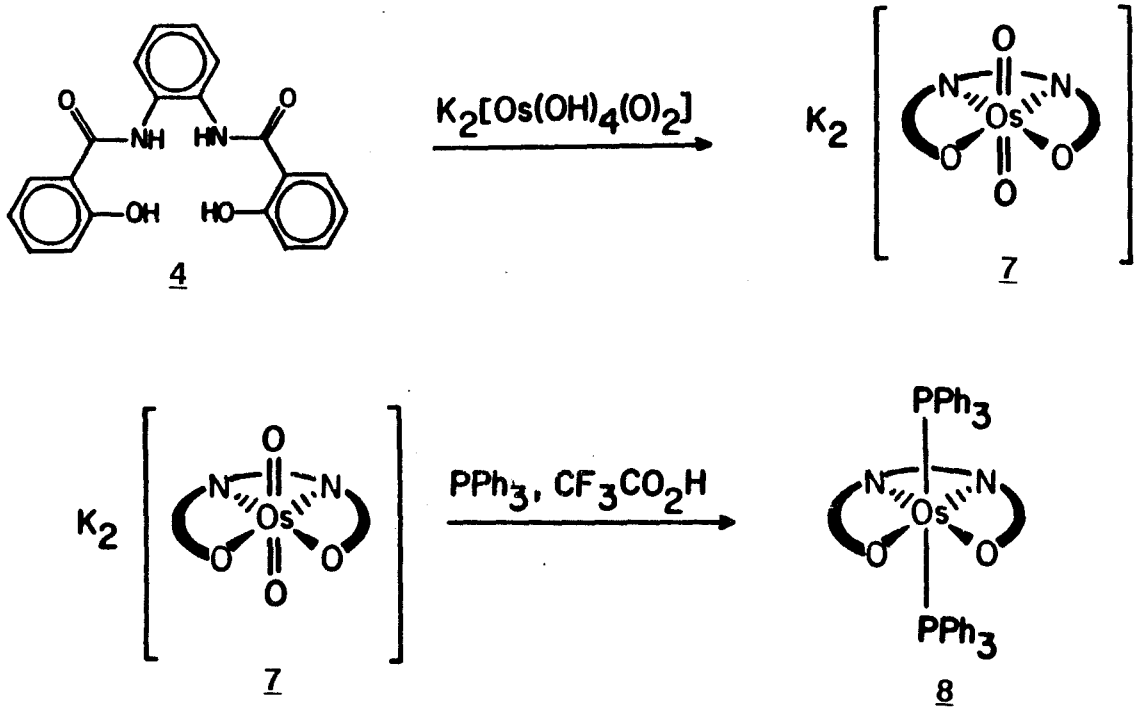
Two equivalents of phenyl azide were added to a degassed benzene solution of 8 under nitrogen at room temperature according to Equation 2.3.



4

H_4HBA-B ≡ 1,2-bis(2-hydroxybenzamido)benzene

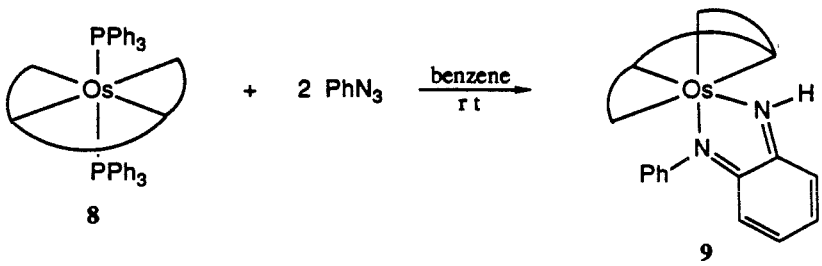
Scheme 2.2. Synthesis of H_4(HBA-B), 4.



4 7 7 8

Scheme 2.3. Synthesis of $[K_2][Os(\eta^4\text{-HBA-B})(O_2)]$, 7, and $Os(\eta^4\text{-HBA-B})(PPh_3)_2$, 8.

(2.3)



8 9

After one hour the green solution turned brown. Thin layer chromatography (TLC) indicated the formation of a new purple compound, the presence of starting material and a brown intermediate complex. The reaction was allowed to continue and over the course of several days became a brilliant deep purple, concomitant with the disappearance of the brown complex. The concentration of the purple product increased steadily for a period of about three weeks. The reaction rate was increased by adding a ten-fold excess of phenyl azide. Heating the reaction mixture produced decomposition. The product was isolated after successive preparative TLC on silica gel plates and elution with methylene chloride. It was necessary to repeat this step several times to achieve an analytically pure sample. Recrystallization from ETOH/hexane afforded deep purple crystals in a 30% overall yield that were suitable for crystallographic study.

Proton NMR spectra showed the expected pattern for the $(\eta^4$-HBA-B$)^{-4}$ ligand (four sets of doublets and two sets of triplets) and a very complicated phenyl region (see Figure 2.3). Despite the absence of infrared (IR) absorption peaks in the characteristic area for transition metal imido complexes (1100-1300cm^{-1})[4], ^{1}H NMR and analytical data led initially to the formulation of the compound as the desired bisimido species, Os$(\eta^4$-HBA-B$)$(NPh)$_2$. A crystallographic study was performed to further elucidate the structure and revealed that in fact the compound was the diimine complex, 9. Proton decoupling and NOE ^{1}H NMR experiments allowed total assignment of the NMR spectrum with the x-ray structure in hand (see Figure 2.3). The ^{1}H NMR spectrum of 9 is an excellent example of a paramagnetic complex that still displays useful NMR spectra. The proton resonances are spread apart by the paramagnetism; the spectrum is actually easier to assign than if the compound were not paramagnetic.

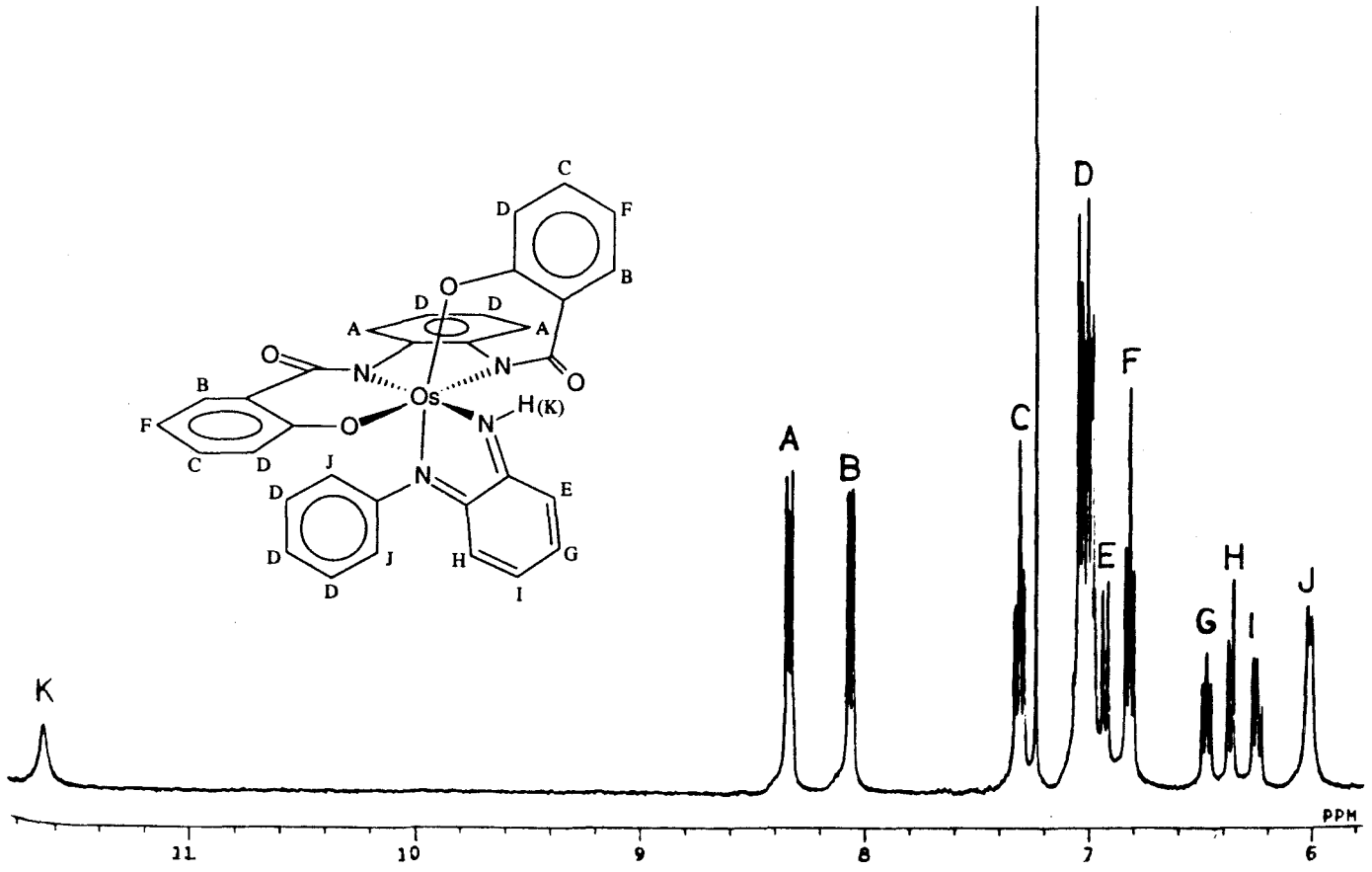


Figure 2.3. ^{1}H NMR spectrum of 9.

X-ray Diffraction Study Of The Diimine Complex, 9

The x-ray structure of the diimine complex, 9 is shown in Figure 2.4 and the bond length data are given in Table 2.3. The ligand is in a *cis*-β arrangement and is twisted out of the planar configuration in response to the structural constraints of the diimine ligand. One of the consequences of the PAC ligand's being in the *cis*-β configuration is that there is considerable rotation around one of the amide C-N bonds (there is a barrier of activation for this rotation of 10-35 kcal/mol)[15], causing a disruption of the amide resonance (pictured in Figure 2.5), and causing the amide to be non-planar.

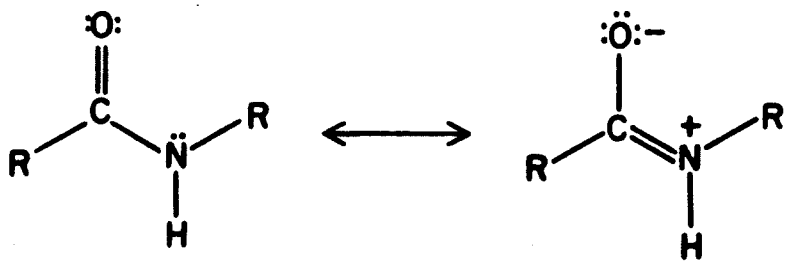


Figure 2.5. Resonance in organic amides

The discovery that the amide is non-planar is an important observation. There are very few non-planar organic amides (examples include formamide,[16] lactams such as penicillin[17] and anti-Bredt bridgehead nitrogen compounds[18]), and the PAC ligand complexes represent the first examples of non-planar amide ligands.

Non-planarity is assessed by a set of parameters, γ, X_c and X_n, first defined by Dunitz and Winkler.[19] γ approximates the angle between the carbonyl carbon p-π orbitals and the unperturbed amide nitrogen and is a measure of the twist around the C-N bond. X_c and X_n measure the out-of-plane bending around the carbon and nitrogen atoms, respectively. Figure 2.6 shows how these parameters are related to the amide torsion angles and can be derived from crystallographic data.

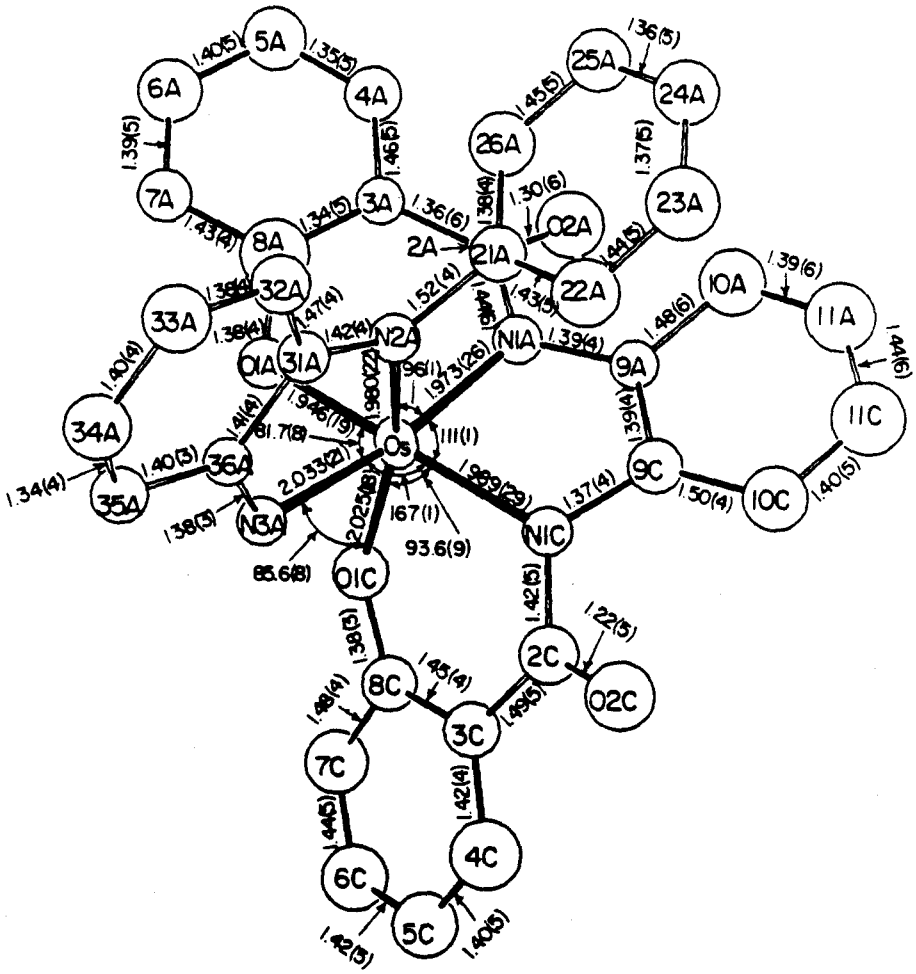
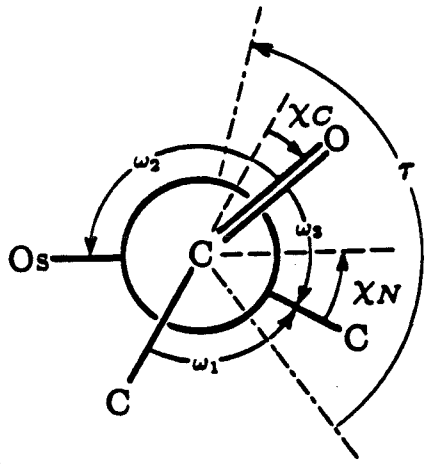


Figure 2.4. Crystal structure of 9.

ATOM	ATOM	DISTANCE	SIGMA	SYM
O51	N1A	1.9732	0.026	0
O51	O1A	1.9457	0.019	0
O51	N1C	1.9889	0.029	0
O51	O1C	2.0255	0.018	0
O51	N2A	1.9801	0.022	0
O51	N3A	2.0327	0.021	0
N1A	[illegible]	1.4448	0.060	0
N1A	[illegible]	1.3940	0.041	0
2A	O2A	1.2972	0.060	0
2A	3A	1.3598	0.063	0
3A	4A	1.4604	0.048	0
3A	8A	1.3372	0.046	0
4A	5A	1.3544	0.050	0
5A	6A	1.3951	0.050	0
6A	7A	1.3889	0.048	0
7A	8A	1.4284	0.045	0
8A	O1A	1.3755	0.037	0
9A	10A	1.4746	0.055	0
9A	9C	1.3892	0.043	0
10A	11A	1.3884	0.064	0
11A	11C	1.4398	0.056	0
N1C	8C	1.4223	0.052	0
N1C	9C	1.3707	0.041	0
2C	O2C	1.2174	0.051	0
2C	3C	1.4893	0.053	0
3C	4C	1.4204	0.043	0
3C	8C	1.4492	0.040	0
4C	5C	1.3977	0.049	0
5C	6C	1.4252	0.050	0
6C	7C	1.4372	0.045	0
7C	8C	1.4850	0.041	0
9C	O1C	1.3745	0.032	0
9C	10C	1.5022	0.044	0
10C	11C	1.3994	0.047	0
N2A	21A	1.5148	0.037	0
N2A	31A	1.4206	0.039	0
21A	22A	1.4329	0.045	0
21A	26A	1.3763	0.043	0
22A	23A	1.4435	0.049	0
23A	24A	1.3650	0.049	0
24A	25A	1.3615	0.048	0
25A	26A	1.4521	0.046	0
31A	32A	1.4678	0.042	0
31A	36A	1.4082	0.040	0
32A	33A	1.3854	0.041	0
33A	34A	1.4027	0.043	0
34A	35A	1.3363	0.037	0
35A	36A	1.3982	0.032	0
36A	N3A	1.3777	0.031	0

ATOM	ATOM	DISTANCE	SIGMA	SYM
O52	N1B	1.9654	0.025	0
O52	O1B	1.9952	0.019	0
O52	N1D	1.9891	0.022	0
O52	N2B	1.9709	0.018	0
O52	N3B	1.9911	0.024	0
N1B	[illegible]	2.0107	0.001 *	32
N1B	[illegible]	1.4391	0.068	0
[illegible]	[illegible]	1.4231	0.041	0
[illegible]	O2B	1.3193	0.049	0
[illegible]	[illegible]	1.3105	0.071	0
[illegible]	[illegible]	1.4244	0.050	0
[illegible]	[illegible]	1.4653	0.049	0
[illegible]	[illegible]	1.4002	0.055	0
[illegible]	[illegible]	1.4158	0.053	0
[illegible]	[illegible]	1.4452	0.048	0
[illegible]	[illegible]	1.4372	0.046	0
[illegible]	O1B	1.3699	0.042	0
[illegible]	10B	1.4539	0.045	0
[illegible]	9D	1.4159	0.045	0
10B	11B	1.4342	0.046	0
11B	11D	1.4013	0.051	0
N1D	8D	1.4674	0.056	0
N1D	9D	1.3782	0.040	0
2D	O2D	1.4610	0.070	0
2D	3D	1.2370	0.072	0
3D	4D	1.4428	0.045	0
3D	8D	1.3997	0.042	0
4D	5D	1.3465	0.049	0
5D	6D	1.4468	0.048	0
6D	7D	1.3396	0.042	0
7D	8D	1.3660	0.040	0
8D	O1D	1.3024	0.034	0
9D	10D	1.4719	0.047	0
10D	11D	1.3730	0.051	0
N2B	21B	1.4591	0.043	0
N2B	31B	1.3696	0.038	0
21B	22B	1.3975	0.045	0
21B	26B	1.3992	0.044	0
22B	23B	1.4325	0.050	0
23B	24B	1.4234	0.048	0
24B	25B	1.4577	0.046	0
25B	26B	1.3765	0.051	0
31B	32B	1.4824	0.043	0
31B	36B	1.3219	0.033 *	2
32B	33B	1.4099	0.043	0
33B	34B	1.5248	0.046	0
34B	35B	1.2736	0.034 *	2
35B	36B	1.4715	0.000 **	32
36B	N3B	1.3748	0.000 *	2

Table 2.3. Bond length data for 9.



$$\tau = ((\omega_1 + \omega_2)/2) \bmod 2\pi$$

$$\chi_N = (\omega_2 - \omega_3 + \pi) \bmod 2\pi$$

$$\chi_C = (\omega_1 - \omega_3 + \pi) \bmod 2\pi$$

Figure 2.6. Projection down the amide C-N bond of a coordinated amide showing the derivation of the angular parameters.

Collins, Peake, *et al.* have defined a new parameter, γ, according to Equation 2.4, such that there is no distinction between the cisoid and transoid geometry.[20]

(2.4) $\gamma = (\gamma) \bmod \pi$

Non-planar amides are defined as those that have a γ value greater than 25°.[20]

Table 2.4 gives the non-planar amide parameters for the diimine complex, 9. As can be seen from these data, complex 9 contains both a planar and a non-planar amide. The γ for the amide that is twisted up into a *cis* configuration is 44, while the amide that remains in the ligand plane has a γ value of only 22°.

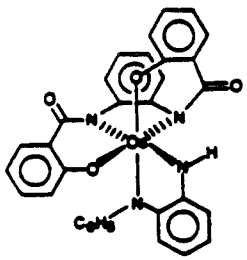
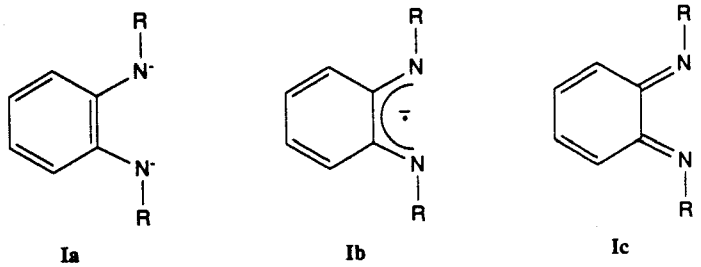
compound	τ (deg)	χ_N (deg)	χ_C (deg)
	22	6	7
	44	-4	-1

Table 2.4 Angular parameters for 9

IR spectroscopy also reflects the configuration of the PAC ligand in the amide CO stretching frequencies. For PAC ligand complexes of 4, that are in a *trans* position, the CO stretching frequencies are ca. 1600cm^{-1}, while the non-planar amide CO stretching frequencies move to lower energy ca. 1650cm^{-1}, as is shown in Figure 2.7.

Another interesting feature of the structure is the ortho-phenylenediimine ligand. The Os-N_2 and Os-N_3 bond distances of 1.98(2)Å and 2.03(2)Å are consistent with the formulation of an osmium-nitrogen single bond. (For example, the Os-N distance in ($Os(NH_3)(Cl_3)(PPh_3)$ is 2.136Å.) The ortho-phenylenediimine ligand has several possible resonance structures, Ia, Ib and Ic, as shown in Figure 2.8.[21]



Ia Ib Ic

Figure 2.8. Resonance structures of the phenylenediimine ligand.

The crystal structure reveals that there is a significant contribution from the diimine form, Ic. The C_{35}-C_{34} (1.33(3)Å) and C_{32}-C_{33} (1.38(4)Å) bonds are somewhat shortened compared to

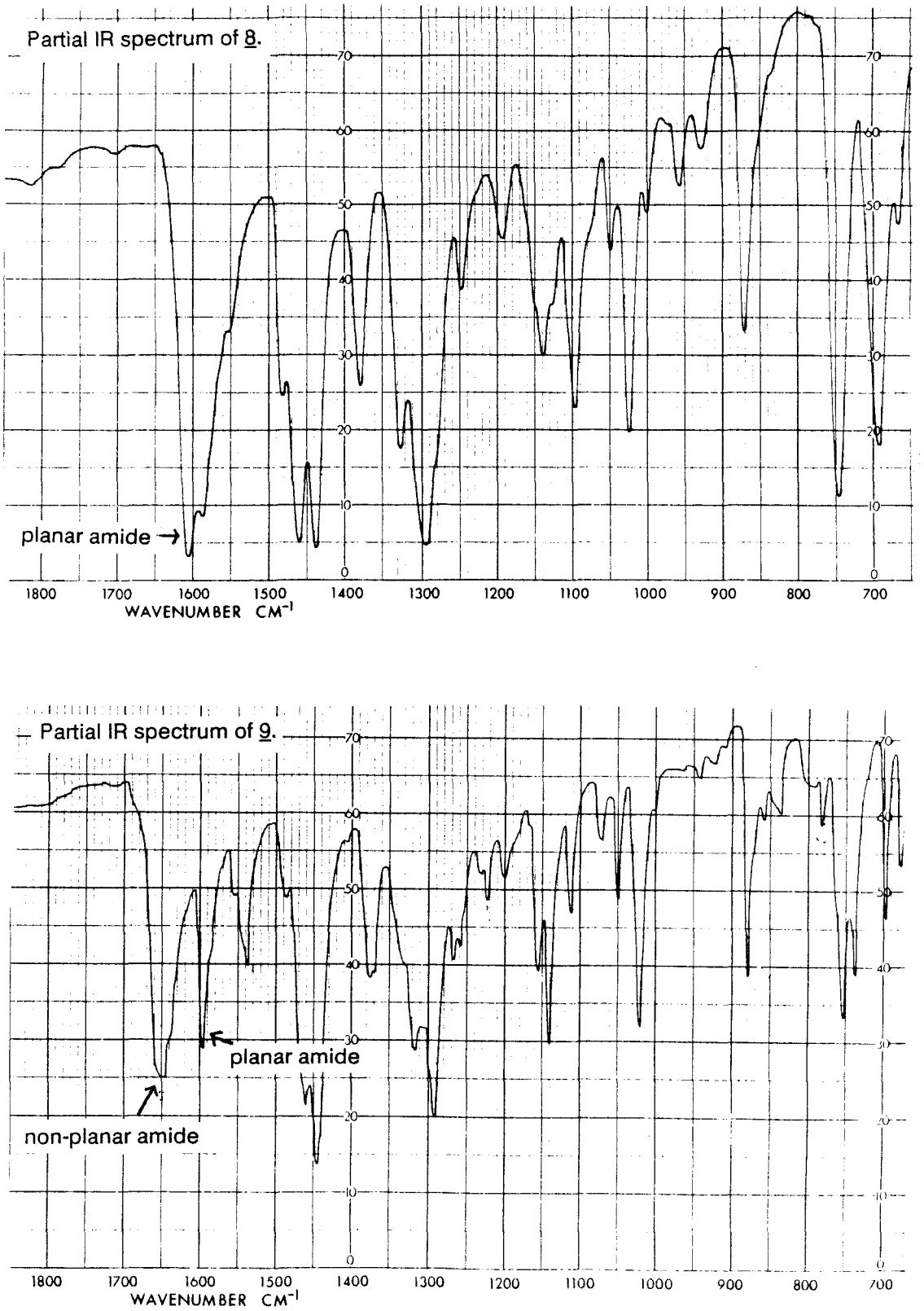


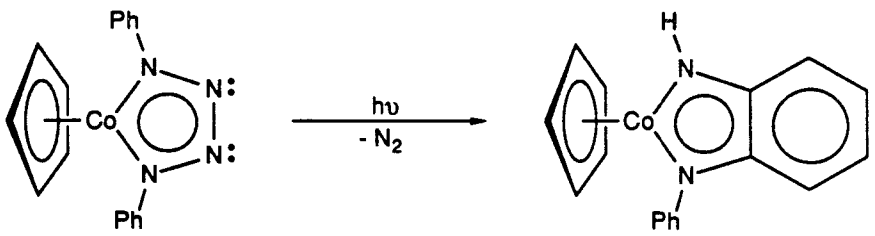
Figure 2.7. A comparison of planar and non-planar amide IR stretching frequencies in 8 and 9.

the other phenylene ring bonds. The N_2-C_{31} (1.42(3)Å and N_3-C_{36} (1.37(3)Å are in between the average N-C single (1.47Å) and average N-C double bond (1.35Å) lengths.

Mechanism

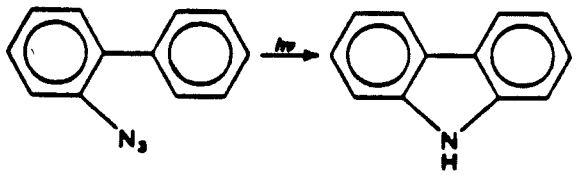
The reaction to form the diimine complex, 9, is not entirely unprecedented. In 1981, Gross, Ibers and Trogler reported the preparation of the diimine complex, 11.[21] This compound was prepared photochemically by extrusion of nitrogen from the starting metallacyclotetraazadiene, 10 (see Equation 2.5).

(2.5)



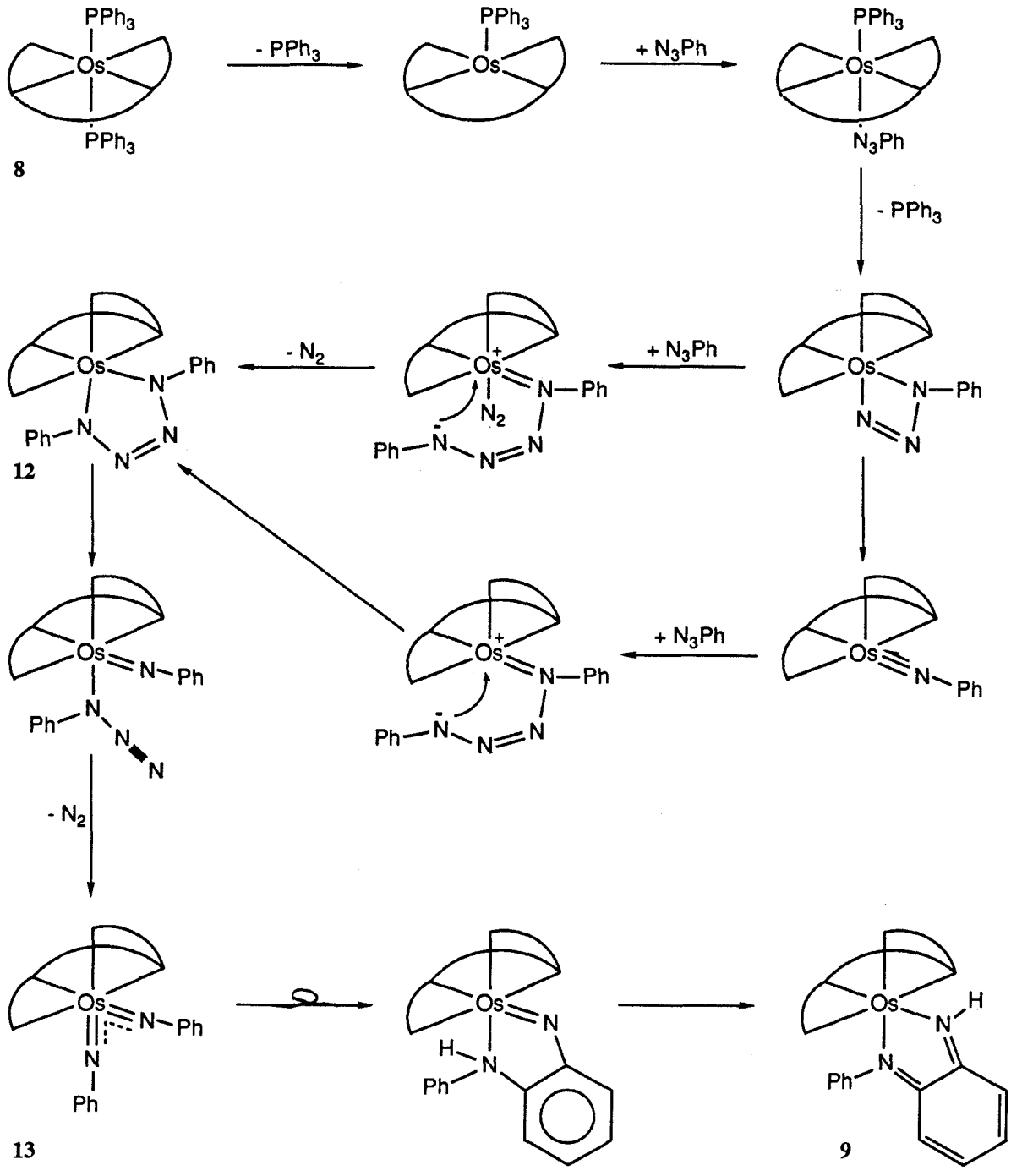
No reaction occurred in refluxing toluene in the absence of light. The diimine product formation requires ortho C-H activation. This step has a precedent in organic photochemistry (see Equation 2.6).[22]

(2.6)



Trogler proposed that the bisimido intermediate complex undergoes insertion (by one of the imido groups) into an ortho C-H bond, which leads to product formation. It is likely that the osmium diimine, 9, is formed via a similar pathway.

The proposed mechanism for the formation of 9 is shown in Scheme 2.4. Parts of this mechanism have been previously reported by Gross and Trogler,[23] Smith, Green and Stone,[24]

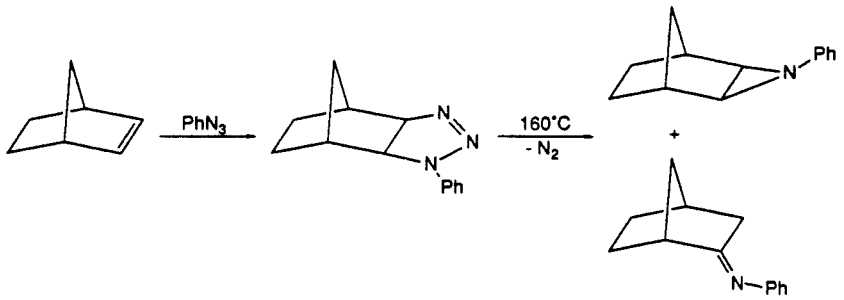


Scheme 2.4. Mechanism of formation for 9.

and Cenini and La Monica.[25] A likely first step is phosphine dissociation from 8. There is a noticeable increase of reaction rate when the starting material is freed from excess triphenylphosphine by washing with copious volumes of hexanes. The phenyl azide could then attack at the vacant coordination site left by the departing phosphine. The strong *trans* influence of the coordinated azide could help push out the other more reluctant phosphine ligand. Isomerization of the ligand would allow bidentate coordination of the azide. The azide can then either extrude nitrogen to form an unsaturated monoimido complex, which could then react with another equivalent of phenyl azide, or alternatively, attack by a second equivalent of azide on the azido complex can precede the nitrogen extrusion step. In either case, the metallacyclotetraazadiene, 12, is formed. Subsequent extrusion of nitrogen from 12 would form the Os(VIII) bisimido species, 13. It is proposed that it is this intermediate that undergoes C-H insertion followed by a 1,3 hydrogen shift to form the final product, 9.

Attempts to isolate and identify the brown intermediate complex which we believe to be the neutral Os(VIII) bisimido species failed because of decomposition and its apparent paramagnetism. During the course of the reaction, which was monitored by TLC by removing aliquots of the reaction mixture at regular intervals, the reaction mixture was cooled to -78 degrees and an attempt was made to isolate the brown intermediate. No meaningful spectra were obtained. Attempts to trap the intermediate or to effect a nitrene transfer *in situ* with a co-reactant also failed. Several olefin substrates were used such as diethyl and dimethyl fumarate and styrene. (Sharpless reported that he was able to isolate the metallacycle bisamido intermediate complex from the reaction of dimethyl and diethyl fumarate with the complexes OsO_xNR_{4-x}).[14] There was evidence of reaction indicated by color change, but no meaningful products could be isolated. The most probable cause is that the olefins can react with organic azides to form either a triazoline or an imine compound, as well as with the metal complex (see Equation 2.7).[26]

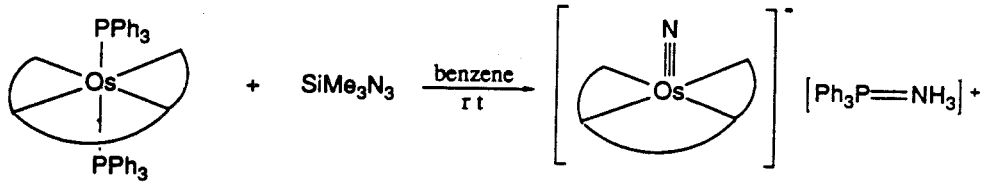
(2.7)



In another attempt to isolate an Os(VIII) bisimido complex, 8 was treated with trimethylsilyl azide. Trimethylsilyl azide was selected because it is commercially available.

Addition of trimethylsilyl azide to a degassed benzene solution of 8 produced an overnight color change from green to straw-yellow (see Equation 2.8).

(2.8)



8 **14**

A pale precipitate fell out of solution, and filtration followed by multiple washings with hexanes produced a yellow powder. Recrystallization from methylene chloride/THF afforded yellow crystals in an overall yield of 80%, suitable for a crystallographic study. The ^{1}H NMR spectrum showed characteristic ligand peaks, aryl phosphine peaks and a noticeable absence of any resonances that could be attributable to a -$Si(CH_3)_3$ group. ^{31}P NMR showed a single resonance at δ+42 ppm attributable to the phosphinimine phosphorous. The IR spectrum exhibited an intense stretch at 1120cm^{-1}, which is in the range of osmium-nitrido stretching frequencies (1123-1023cm^{-1}).[4] The structure was assigned as the Os(VI) nitrido compound, 14; this was confirmed by the x-ray crystallographic study.

X-ray Diffraction Study Of The Nitrido Complex, 14

Osmium has the most extensive nitrido chemistry of all the transition metals.[4] Most of the osmium nitrido complexes known are Os(VI) species. The most salient feature of the nitrido ligand is its very strong π-donor capability. Bond length data, force constants, *trans*-effect

studies and electronic spectra indicate that it is the strongest π-donor known.[4] The crystal structure shown in Figure 2.9 illustrates this point. The bond length data are given in Table 2.5. The Os-N distance is 1.64(1) Å, which is the expected distance for an Os-N triple bond as compared to $[K_2][OsNCl_5]$ (OS-N,1.614 Å) and $[Ph_4As][OsNCL_4]$ (Os-N, 1.60 Å). In contrast, the Os-N single bond distance is 2.136 Å in $Os(NH_3)(Cl_3)(PPH_3)_2$ and the calculated Os-N double bond distance is 1.77 Å.[3] An interesting feature of this compound is that the osmium sits up out of the ligand plane by 0.56Å, with an average N-Os-L angle of 106.4°, which is a greater distortion than is usually seen. For example, $OsCl_4N^-$ and $OsCl_5N^{-2}$ have N-Os-L angles of 104.5° and 96°, respectively.[27] Belmonte has reported a $[NBu_4][Os(N)R_4]$ compound that also exhibits a large distortion: the average N-Os-C bond angle is 107.7°.[28] Dubois and Hoffmann have done orbital calculations on nitrido complexes and suggest that this distortion out of the basal plane is caused by the stabilization of the 2e set of orbitals with increasing N-M-L angle.[29] The ligand bending causes increased overlap between the p orbitals on the nitrogen and the metal xz and yz orbitals. A more complete discussion of this follows in a later section.

The amide ligand linkages are both non-planar, a highly unusual occurrence (*vide supra*). The γ, X_n and X_c values for 14 are shown in Table 2.6.

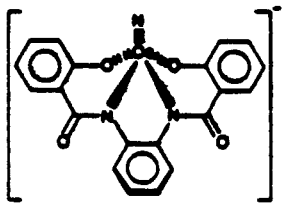
compound	γ (deg)	χ_N (deg)	χ_C (deg)
	30 5	25 7	3 0

Table 2.6. Angular parameters for 14

The IR data again reflect the non-planarity of the amides, and the carbonyl stretches are found at 1637cm^{-1} (vs. ca. 1600cm^{-1} for planar amides). It is assumed that the non-planarity of the

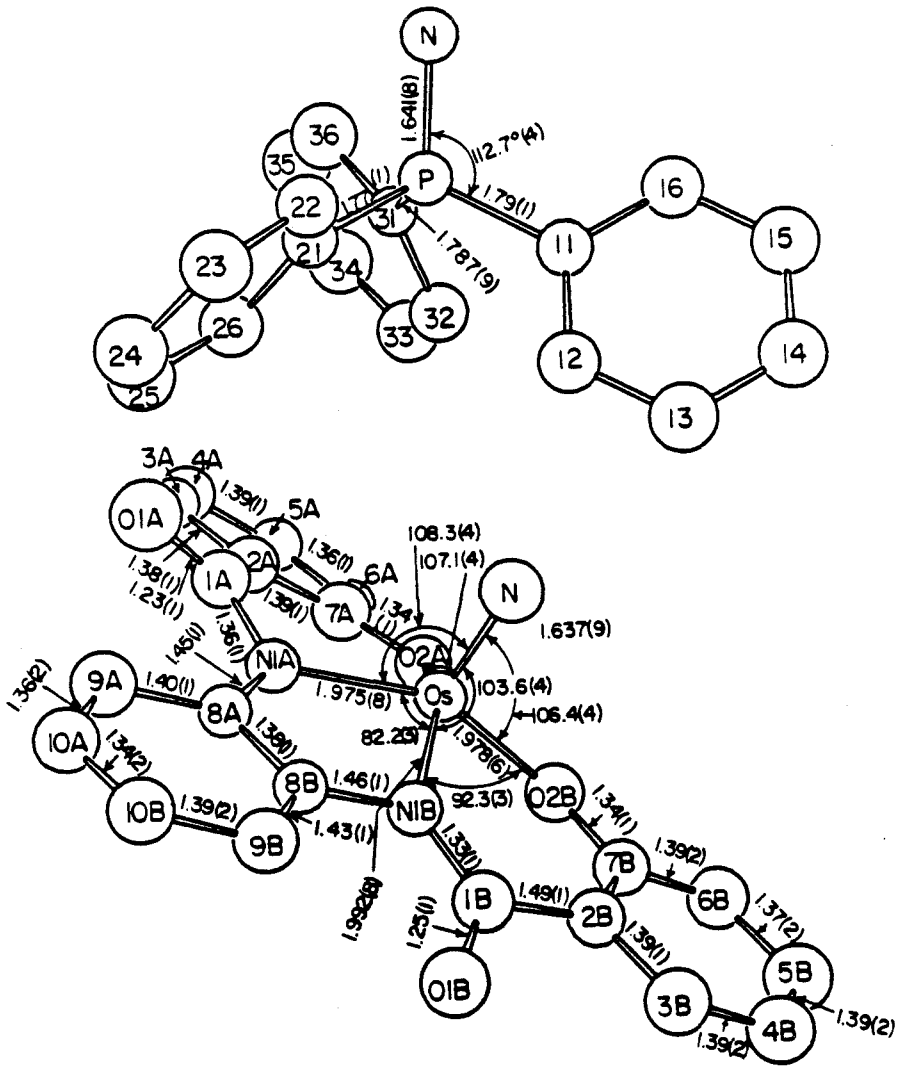


Figure 2.9. Crystal structure of 14.

ATOM	ATOM	DISTANCE	SIGMA	SYM
O5	X	1.4402	0.010	0
O5	N1A	1.9834	0.009	0
O5	O2A	1.9262	0.007	0
O5	N1B	1.9959	0.009	0
O5	O2B	1.9734	0.008	0
N1A	1A	1.3540	0.015	0
N1A	8A	1.4703	0.014	0
O1A	1A	1.2374	0.015	0
O2A	7A	1.3313	0.014	0
1A	2A	1.5159	0.017	0
2A	3A	1.4044	0.017	0
2A	7A	1.3696	0.017	0
3A	4A	1.3615	0.017	0
4A	5A	1.4283	0.017	0
5A	6A	1.3778	0.016	0
6A	7A	1.4495	0.016	0
8A	9A	1.4387	0.017	0
8A	8B	1.3601	0.016	0
9A	10A	1.4103	0.018	0
10A	10B	1.3347	0.018	0
N1B	1B	1.3285	0.015	0
N1B	8B	1.4603	0.014	0
O1B	1B	1.2300	0.015	0
O2B	7B	1.3506	0.014	0
1B	2B	1.4658	0.017	0
2B	3B	1.4168	0.018	0
2B	7B	1.4035	0.017	0
3B	4B	1.3758	0.019	0
4B	5B	1.4167	0.019	0
5B	6B	1.4114	0.019	0
6B	7B	1.4122	0.018	0
8B	9B	1.4583	0.017	0
9B	10B	1.4384	0.018	0
P	N	1.6410	0.010	0
P	11	1.7793	0.012	0
P	21	1.7759	0.011	0
P	31	1.7928	0.010	0
11	12	1.3993	0.017	0
11	16	1.4016	0.016	0
12	13	1.4141	0.018	0
13	14	1.4167	0.018	0
14	15	1.3679	0.018	0
15	16	1.4056	0.017	0
21	22	1.4238	0.016	0
21	26	1.4471	0.016	0
22	23	1.4294	0.018	0
23	24	1.3811	0.019	0
24	25	1.4019	0.019	0
25	26	1.4034	0.018	0
31	32	1.4281	0.014	0
31	36	1.3846	0.017	0
32	33	1.4010	0.018	0
33	34	1.3824	0.019	0
34	35	1.4219	0.020	0
35	36	1.4355	0.020	0

ATOM	ATOM	ATOM	ANGLE	SIGMA	SY1	SY3
N1A	O5	X	107.24	0.435	0	0
O2A	O5	X	107.97	0.417	0	0
N1B	O5	X	104.16	0.436	0	0
O2B	O5	X	106.30	0.418	0	0
O2A	O5	N1A	69.75	0.341	0	0
N1B	O5	N1A	82.47	0.369	0	0
O2B	O5	N1A	146.32	0.344	0	0
N1B	O5	O2A	147.81	0.342	0	0
O2B	O5	O2A	77.05	0.314	0	0
O2B	O5	N1B	92.33	0.344	0	0

Table 2.5. Bond length data for 14.

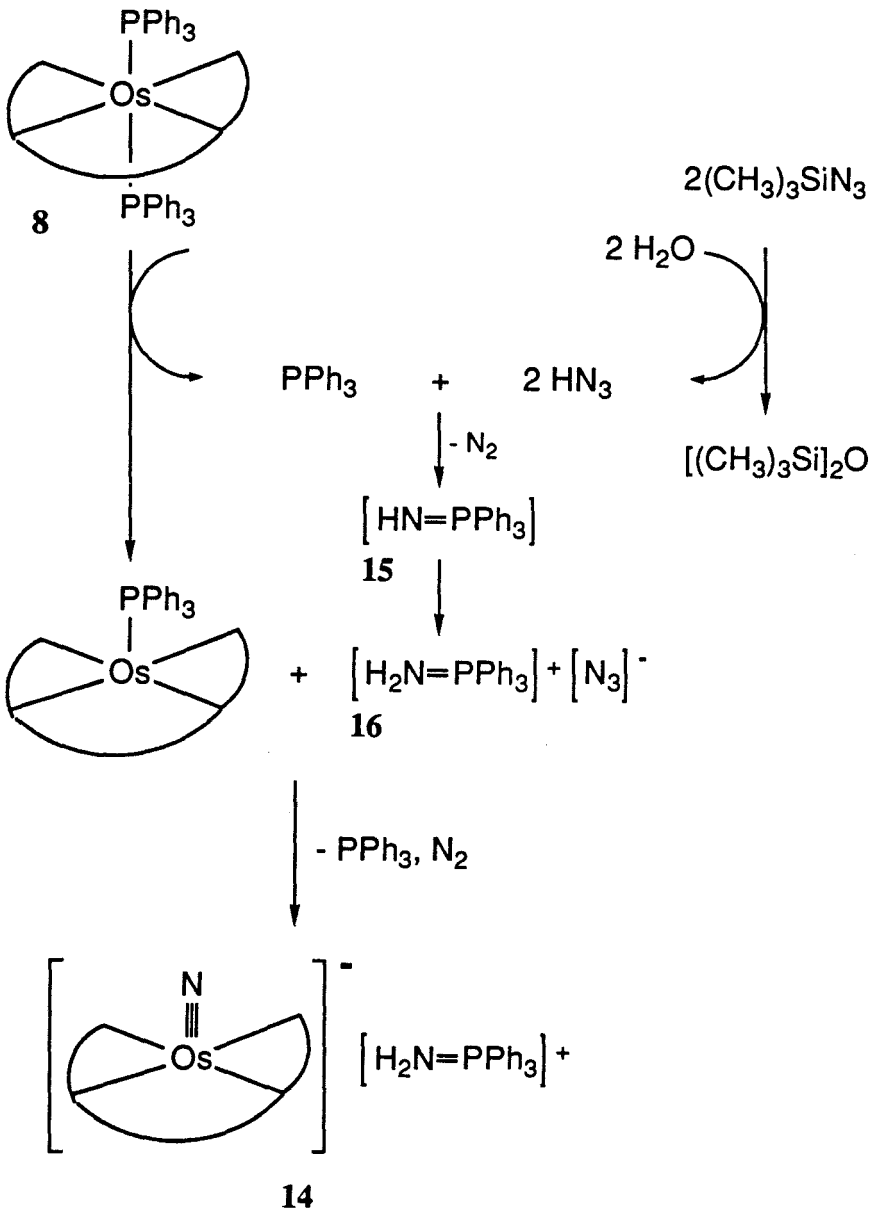
PAC ligand amide groups (a direct result of the osmium atom sitting up out of the plane) reflects the electronic requirements of the Os(VI) metal center. Presumably, the increased overlap of the metal xz and yz orbitals with the nitrogen p orbitals, combined with the increased donating ability of the non-planar amides, allows this formally Os(VI) compound to "feel" electron-rich at the metal center.

The counterion, $H_2N{=}PPh_3^+$, of the nitrido complex is also fairly unusual. The P-N bond distance is 1.64(1) Å, which is in good agreement with a P-N double bond (for example, P=N = 1.567 Å for $PPh_3{=}NPh$-*p*-Br and P=N = 1.641 Å for Ph_2 $FP{=}NCH_3$).[30] The hydrogens on the nitrogen were not located. The other ligand bond distances do not show any unusual features.

Mechanism

Thermal decomposition of chloroazide (ClN_3) or NaN_3 in HX is a well known method for nitrido synthesis.[4] This reaction is the first example of a fully characterized nitrido complex formed from the decomposition of an organic azide, although Chatt and Dilworth have also reported the preparation of an uncharacterized "Mo=N" species from $(CH_3)_3SiN_3$.[31]. A suggested mechanism for the formation of 14 is shown in Scheme 2.5. A probable first step is the hydrolysis of $(CH_3)_3SiN_3$ to form the parent azide, hydrozoic acid (HN_3). The $-Si(CH_3)_3$ group is known to hydrolyze under mild conditions. As previously mentioned, the complex can readily dissociate one of the triphenylphosphine ligands. At this point the parent azide could undergo a Staudinger reaction with dissociated PPh_3 to form the phosphinimine, 15, which is known to further react with the hydrazoic acid to produce the ion pair, 16. The azide ion, N_3^-, is then free to attack the unsaturated osmium complex, extrude nitrogen and form the final product, 14.

Attack by free azide ion has been proposed by several groups for the formation of Re(V), Re(III),[32] Mo(VI),[33], Ru(VI) and Os(VI)[6] nitrido complexes. The following evidence supports this mechanism:



Scheme 2.5. Mechanism of formation for 14.

(1) The reaction proceeds faster when the starting material is free from excess PPh_3, suggesting that phosphine dissociation from 8 is involved.

(2) $(CH_3)_3SiN_3 + PPh_3 \not\longrightarrow (CH_3)_3SiN{=}PPh_3$ (15)

This reaction is the well-known Staudinger reaction.[34] Phosphines and azides will react to form phosphinimines quite readily and under a variety of conditions; however, this reaction does not occur at room temperature.

(3) $(CH_3)_3SiN{=}PPh_3$ (15) + 8 $\not\longrightarrow$ 14

The phosphinimine reagent, 15, was independently prepared and does not react with the starting material, 8, to form the final product, 14.

(4a) $(CH_3)_3SiN{=}PPH_3$ (15) + H_2O/benzene $\longrightarrow$ NR

(4b) $(CH_3)_3SiN{=}PPh_3$ (15) + $CH_3OH/H^+ \longrightarrow [HN{=}PPh_3\} \longrightarrow H_2N{=}PPh_3$

15 does not decompose to the parent phosphinimine under the reaction conditions, but requires acid and a polar solvent.[34]

(5). $(CH_3)_3SiN_3$ + H_2O/benzene $\longrightarrow$ HN_3 + $((CH_3)_3Si)O_2$

This reaction *will* occur under the reaction conditions. The products were identified by ^1H NMR.

(6a). $HN_3 + PPh_3 \longrightarrow HN{=}PPh_3$

(6b). $HN{=}PPh_3 + HN_3 \longrightarrow [H_2N{=}PPh_3]^+$

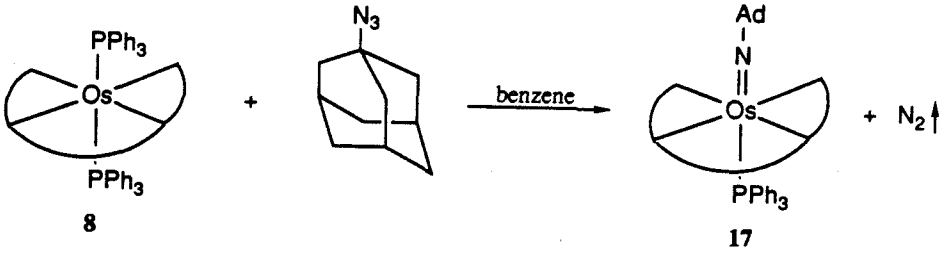
This reaction is also a Staudinger reaction that will occur under the reaction conditions.[34] Note: a reaction that should be performed is the treatment of 8 with HN_3 to determine if 14 is produced.

(7). The mother liquor of the reaction shows a new ^1H NMR peak that can be assigned to $(Me_3Si)_2O$. (The literature value is +0.1 ppm.) $(Me_3Si)_2O$ (independently prepared) was added to the mother liquor and the peaks were found to coincide. In addition to the NMR evidence, the IR spectrum of the neat mother liquor shows bands corresponding to $(Me_3Si)_2O$.

Both the aromatic azide (phenyl azide) and the heteroatomic azide (trimethylsilyl azide) failed to yield the desired bisimido complex. The next logical choice of azide is an aliphatic hydrocarbon. Reactions with several aliphatic azides were explored: 1-adamantyl azide, methyl azide, t-butylazido formate and trityl azide.

1-adamantyl azide is commercially available. 8 was stirred overnight at room temperature with an excess of 1-adamantyl azide in benzene according to Equation 2.9.

(2.9)



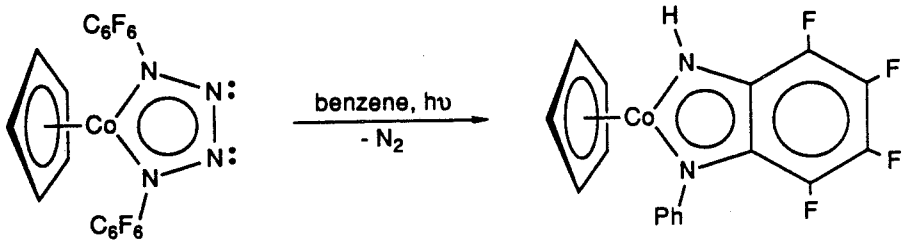
The solution slowly changed from green to a chocolate brown. TLC showed that the reaction was not completely clean. Preparative TLC by elution with 3:1 methylene chloride/acetone allowed the collection of a brown compound, the major product (ca. 60%). However, several successive TLCs were necessary to isolate the compound in a pure state, and the overall yield dropped to 10%. The ^1H NMR spectrum showed ligand peaks in the appropriate downfield region, along with triphenylphosphine resonances. Adamantyl resonances not corresponding to the starting azide were present in the aliphatic region. The integrations were consistent with a formulation of 1:1:1 in the PAC ligand, adamantyl group and triphenylphosphine. The ^{31}P

NMR spectrum showed one new resonance at δ+34 ppm. The IR spectrum exhibited a strong absorption at 1150 cm^{-1}, which is in the correct region for metal-imido aborptions (1100-1300cm^{-1}).[3] The analysis was acceptable for the monoimido osmium PAC ligand phosphine complex, 17. Unfortunately, x-ray quality crystals were never obtained as the compound decomposed. The adamantylimido complex is only the second adamantylimido complex that has been reported. Sharpless prepared the compound $Os(NR)_2(O)_2$, where R=1-adamantyl. There is an Os=NR IR peak at 1160cm^{-1}. This reagent was demonstrated to be active in the ammoxidation of olefins.[35] Because the complex 17 was somewhat intractable and could be obtained only in low yield, no further reactivity studies were undertaken.

The other aliphatic azides, methyl azide, t-butylazido formate and trityl azide did not produce clean reactions and were not pursued.

In another attempt to produce a bisimido complex, perfluorophenyl azide was selected as a reactant because it was expected that by substituting fluorine for hydrogen and thus eliminating the possibility of C-H insertion, it would be possible to isolate the bisimido complex. However, Gross and Trogler reported a remarkable C-F insertion in a similar system to that discussed above (see Equation 2.10).[36]

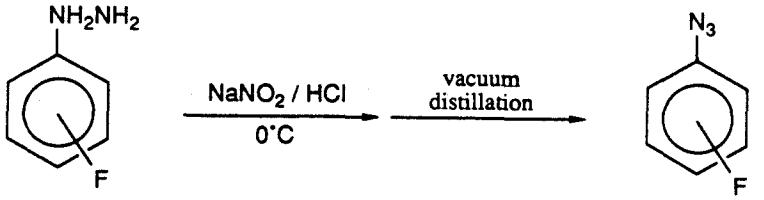
(2.10)



He was unable to determine the source of the proton on the diimine ligand but speculated that the source was from a free radical reaction with the protiated solvent.

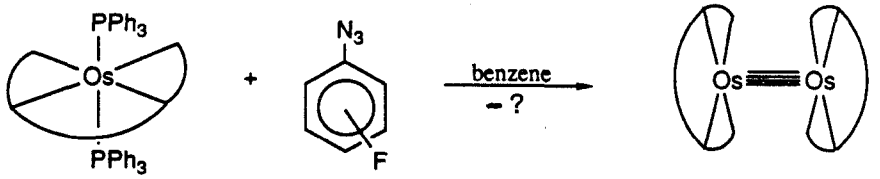
Perfluorophenyl azide was prepared according to literature methods, as shown in Equation 2.11.[37]

(2.11)



8 was stirred overnight in benzene with an excess of perfluorophenyl azide according to Equation 2.12.

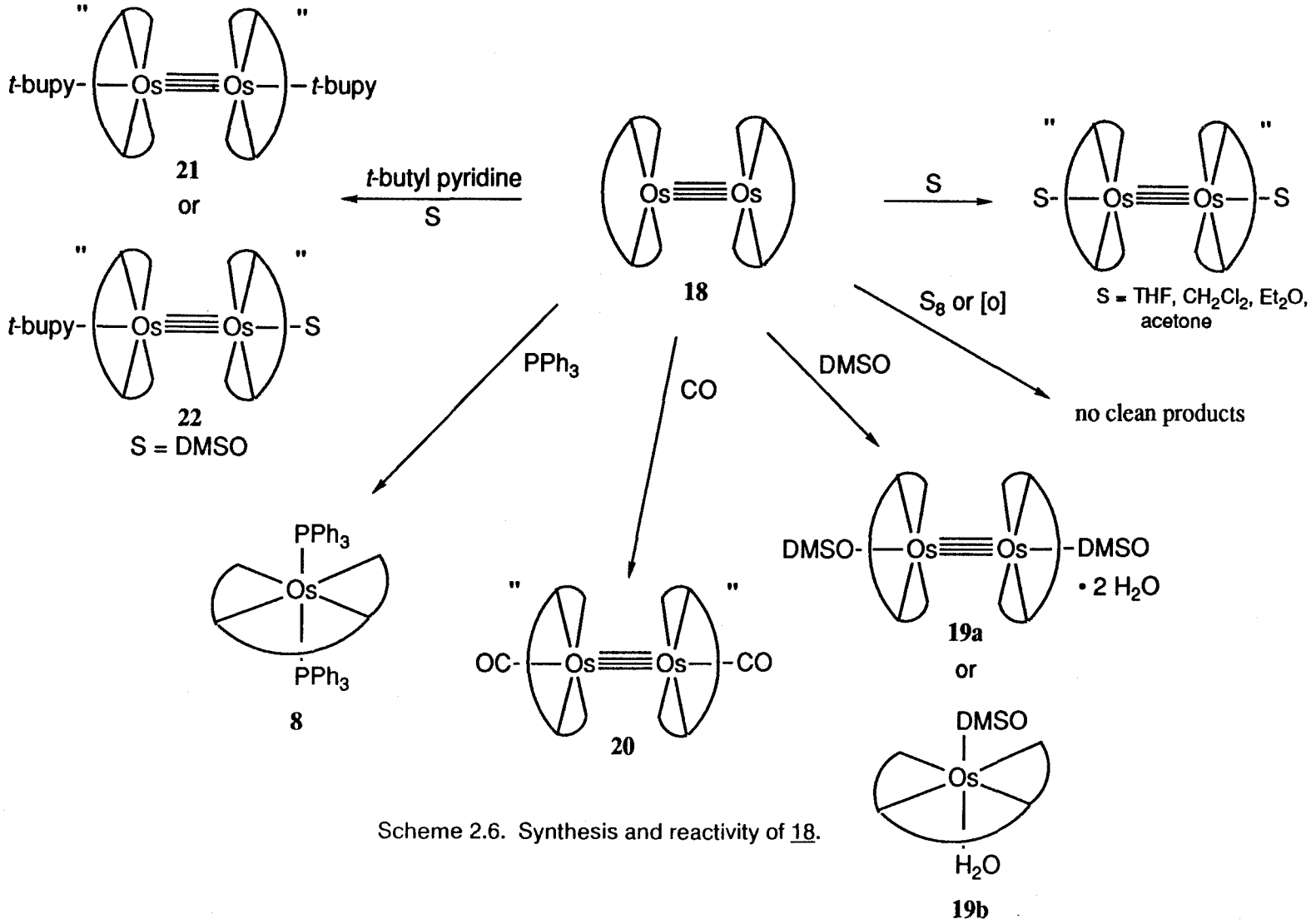
(2.12)



8 **18**

The solution gradually changed from green to black, and a black precipitate fell out of solution. TLC showed the reaction to be relatively clean with essentially one (baseline; R_f=0) component. The black precipitate did not dissolve readily in solvents with the exception of hot DMSO in which it formed a black-purple solution. However, if the black powder was allowed to remain for a long period of time (e.g., overnight) in a solvent such as diethylether, THF, methylene chloride or acetone, it dissolved slowly to form purple compounds that had an R_f of approximately .8. These compounds were subsequently soluble in benzene. There were no ^{1}H NMR spectra associated with any of these compounds. However, the black-purple solution of DMSO was pumped to dryness *in vacuo*, after which the compound was also soluble in benzene. It was possible to obtain an ^{1}H NMR spectrum of this compound in DMSO-d_6. The spectrum showed only PAC ligand resonances along with DMSO and water resonances in a 1:1:1 ratio. The IR of this compound exhibited absorption peaks in the region of O-bound DMSO complexes (925,940 cm^{-1})[38] as well as characteristic water peaks.

This anomalous compound is tentatively formulated as the Os-Os multiply-bonded PAC ligand dimer, 18 (see Scheme 2.6), on the basis of its behavior towards solvents, ligands and the spectroscopic evidence presented below. It is most reasonable to formulate the multiple



Scheme 2.6. Synthesis and reactivity of 18.

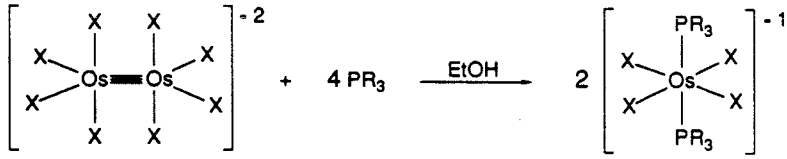
bond as quadruple for reasons that will be explained (*vide infra*). Microanalysis of the original black powder (18) before any solvents have been added is in agreement with this formulation. 18 is apparently capable of coordinating other solvent molecules into the two vacant coordination sites (see Scheme 2.6). ^{1}H NMR spectra and microanalytical data after the black compound has been dissolved in hot DMSO lead to the formulation of the compound as [Os(η^4-HBA-B)(DMSO)·H_2O]$_x$, 19a or 19b (where x = 1 or 2). It is not possible to distinguish between these two possible structures shown in Scheme 2.6.

The reaction of 18 with triphenylphosphine supports the formulation of 18 as the dimeric species. When 18 was stirred in benzene with triphenylphosphine at room temperature, it converted cleanly back to the green monomeric starting material, 8 (see Scheme 2.6). There was no evidence at all by TLC, or from the examination of the entire reaction mixture by ^{1}H NMR, that any other side product was present.

18 was also treated with *t*-butylpyridine in benzene at room temperature overnight to form a purple compound. The reaction was not very clean, and a pure sample for microanalysis and ^{1}H NMR spectroscopy was difficult to obtain even after repeated preparative TLC (elution with methylene chloride) steps. The compound appeared to be paramagnetic; the ligand and *t*-butylpyridine peaks were quite spread out, and the integration of the *t*-butylpyridine peaks was only half of what was needed for the osmium dimeric complex, 21. It may be that upon workup one of the *t*-butylpyridine ligands was replaced by another solvent molecule (such as DMSO), or that only one *t*-butylpyridine ever coordinated and that the other site was occupied by a solvent in the subsequent workup procedure, *i.e.*, 22. The compound Os(η^4-HBA-B)$(PPh)_3$(*t*-Bupy), which was prepared by stirring 8 in *t*-butylpyridine, was also found to be paramagnetic with a wide range of ^{1}H resonances.[8] It was not possible to substitute both phosphines for *t*-butylpyridine by this method, so there is no direct comparison available. The IR spectra for 21 (or 22) was similar to the spectrum of Os(η^4-HBA-B)(PPh_3)(*t*-Bupy). There was an electronic absorption band at 771 nm (12,970 cm^{-1}), which could mean that the osmium-osmium bond is intact (*vide infra*).

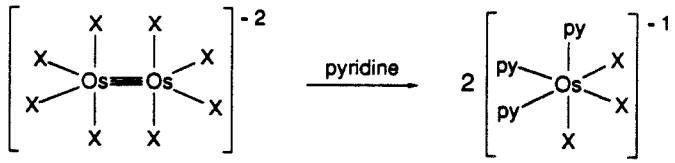
Walton has reported that when the Os-Os multiply-bonded complexes, $[Os_2X_8]^{-2}$, are treated with phosphorous (PR_3) and nitrogen (pyridine) donor ligands the metal-metal bond is cleaved (see Equation 2.13a and 2.13b).[39]

(2.13a)



X = Cl, Br; PR_3 = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$

(2.13b)



X = Cl, Br

It may be that in the case of 18, the stronger σ-donation of the PR_3 ligand is required to cleave the Os-Os quadruple bond and that the *t*-butylpyridine ligand simply isn't a strong enough donor to cleave the Os-Os bond.

The proposal that the black compound is an Os-Os quadruply-bonded dimer presents an interesting possibility. There are many examples of Mo-Mo and Re-Re quadruply-bonded dimeric compounds.[40] Despite the fact that the Os(IV) metal centers (d^4-d^4) are isoelectronic with Cr(II), Mo(II), W(II) and Re(III) all of which form quadruply-bonded species, no examples of Os-Os quadruple bonds have appeared in the literature.[40] In fact, even examples of well-characterized Os(III) (d^5-d^5) triply-bonded dimers are limited to $[Os_2X_8]^{-2}$ and $Os_2(hp)_4Cl_2$ (where hp= 2-hydroxypyridine).[39,41] In addition to these examples, Collman has proposed a triple bond in the metalloporphyrin complex $[Os(OEP)]_2$ (where OEP= octaethylporphyrin).[42]

Electronic absorption spectra of compounds with multiple M-M bonds have been extensively examined.[43] For the metal dimeric compounds with an electronic configuration of $\sigma^2\pi^4\delta^2$ (this includes Os(IV)-Os(IV)), the lowest energy electronic transition should be the δ-δ^* transition.[40] The relative energies of the molecular orbitals for a M_2L_8 compound with a ground state of d^4-d^4 are shown in Figure 2.10. The δ-δ^* transition has been observed to occur between the near-IR (ca. 16000nm) and the middle of the visible range (ca. 450nm) in all cases

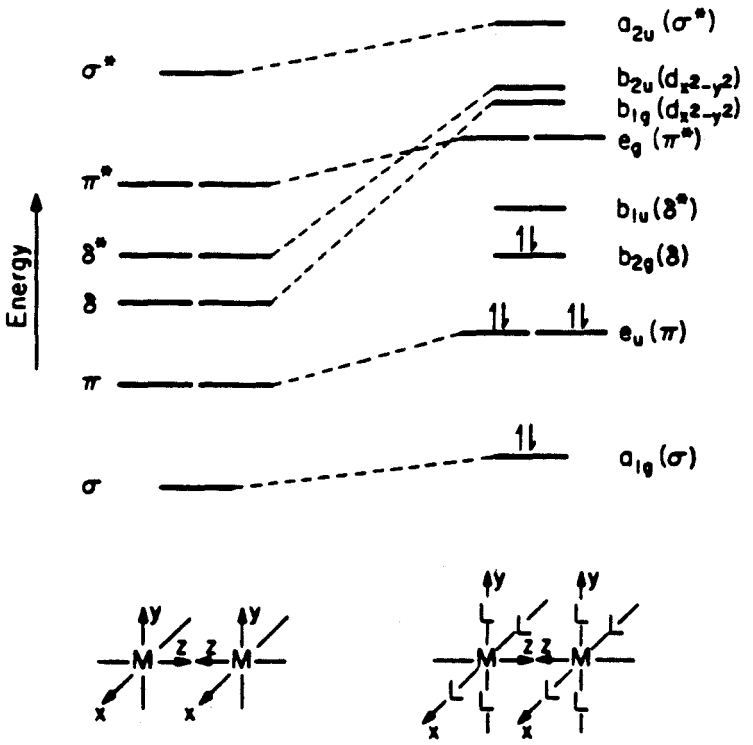


Figure 2.10. Relative energies of the molecular orbitals for a M_2L_8 compound with a d^4-d^4 ground state.

where this ground state configuration exists.[40] Two general trends for these transitions are reported: the intensities are quite low because of the small overlap of the two d orbitals that make up the δ bond, and the transition is always observed at a far higher energy than can be calculated.[40,43] Although conclusions drawn from the electronic absorption spectra should be supported by x-ray crystallography, it is interesting to note that 18 does show absorptions in the region where M-M multiple bonds are found. The electronic absorption spectrum of 18 is shown in Figure 2.11 and has an absorption band at 768 nm (13,200 cm^{-1}) in methylene chloride; the absorption spectrum is identical when it is taken in toluene. (The solutions were prepared and used quickly to prevent reaction with the solvent, but when they were examined several hours later, there was no change.) Figure 2.12 shows the spectrum of the DMSO compound, 19, which also displays a band at 775 nm (12,903 cm^{-1}) in methylene chloride. The spectrum of 19 that has been stirred in THF also shows an absorption in this region, at 712 nm (14,044 cm^{-1}). An analogous quadruply-bonded rhenium-rhenium compound, $Re_2Cl_8^{-2}$ exhibits a δ-δ^* absorption band at 14,654 cm^{-1}.[43] The lower wave number of the absorption band for 18 is consistent with osmium being a heavier element. The electronic spectrum of the starting monomeric complex, 8, shows no absorption band in this region.

Metal-metal quadruply-bonded complexes have a characteristic vibronic stucture in the δ-δ^* band, as a consequence of metal-metal stretching, that can be seen at low temperature. Accordingly, the low temperature (77°K) electronic absorption spectrum was obtained as a 2-methyltetrahydrofuran glass and clearly showed vibronic structure (see Figure 2.13a). The shape of the band is similar to the shape of the low-temperature (5°K) spectrum of $Re_2Cl_8^{-2}$ (see Figure 2.13b) and is characteristic of δ-δ^* excitations into a σ antibonding orbital.[43] The bond order of the metal-metal bond is reduced, causing a "displacement-shift" of the potential energy wells (along some coordinate axis). This displacement makes it likely that the strongest absorption would be at higher energy (*i.e.,* 0-4 *versus* 0-1; see Figure 2.13a). This pattern is observed for $[Re_2Cl_8]^{-2}$ and for 18. The vibronic structure that is observable at low-temperature for 18 has an average progression of 305 cm^{-1}, which is in the middle of the known range (250

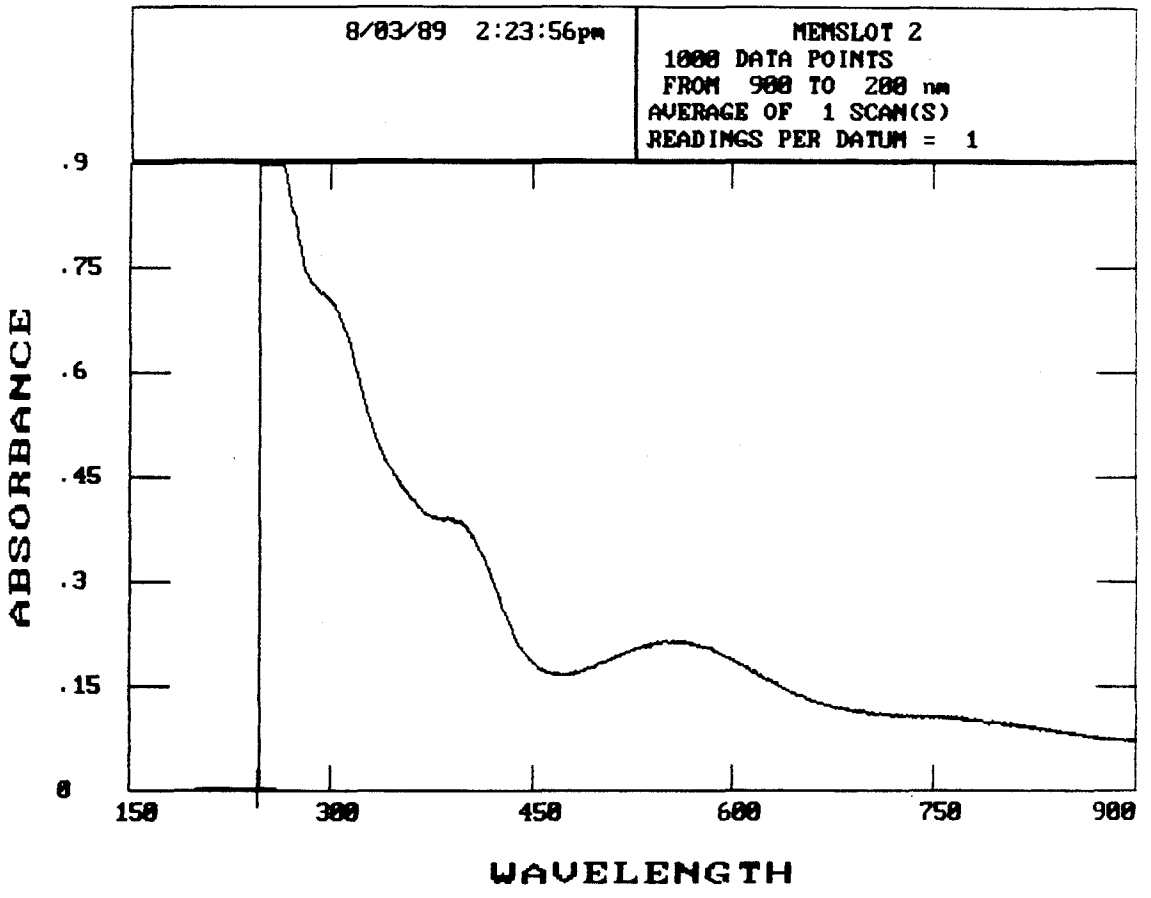


Figure 2.11. Electronic absorption spectrum of 18 in methylene chloride.

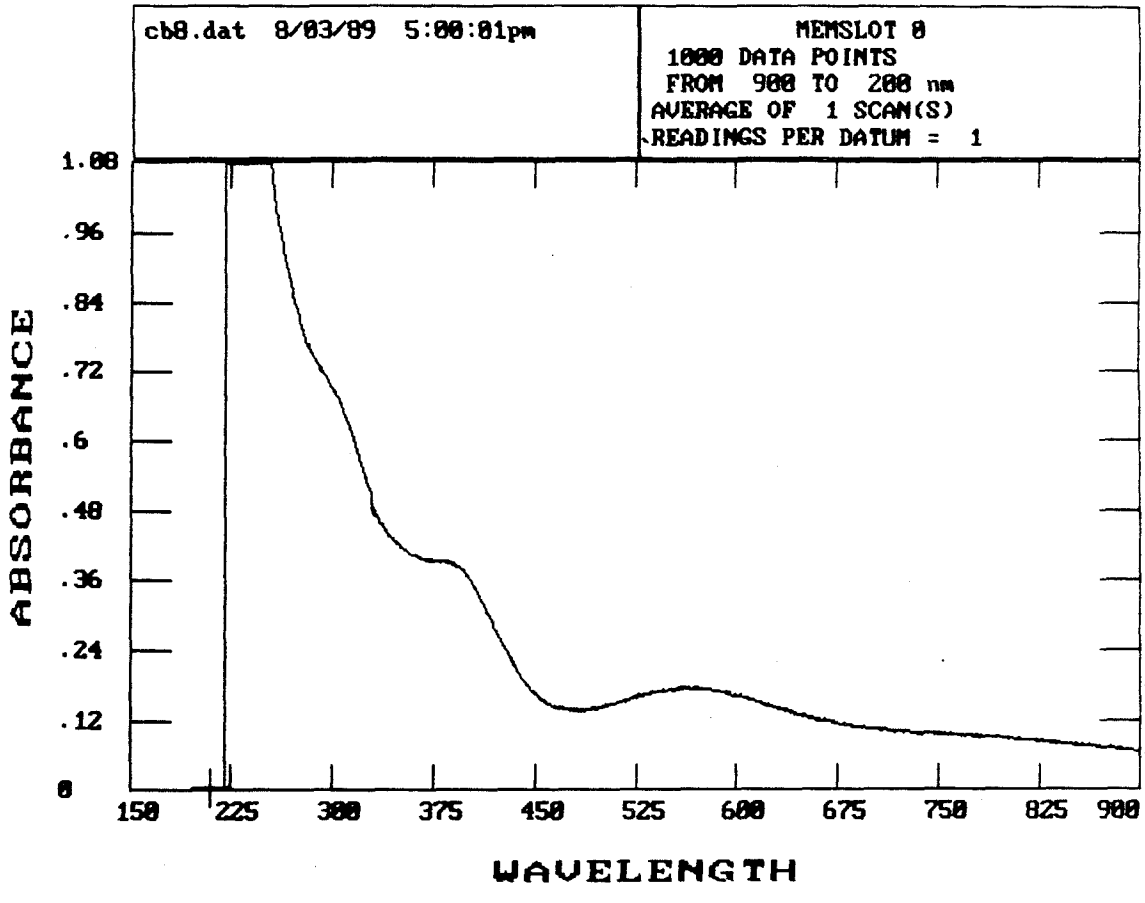


Figure 2.12. Electronic absorption spectrum of 19 in methylene chloride.

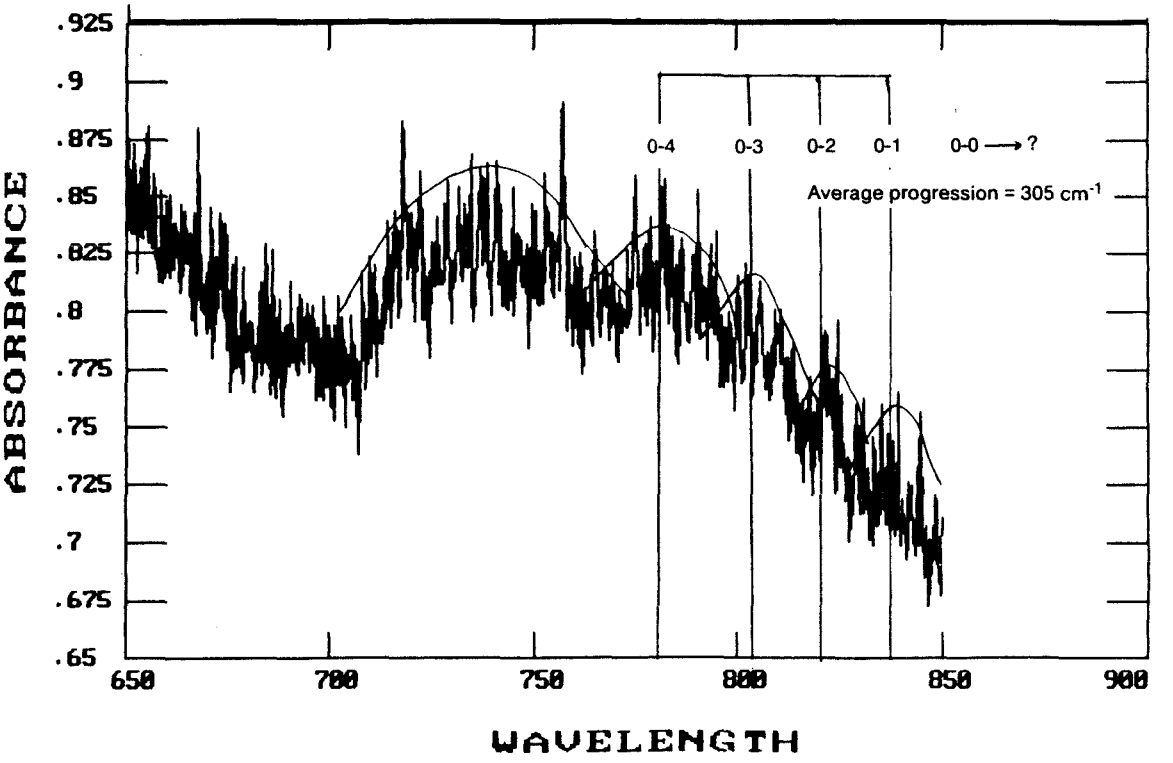


Figure 2.13a. Electronic absorption spectrum at 77°K of 18 showing the vibronic structure of the δ-δ^* transition band.

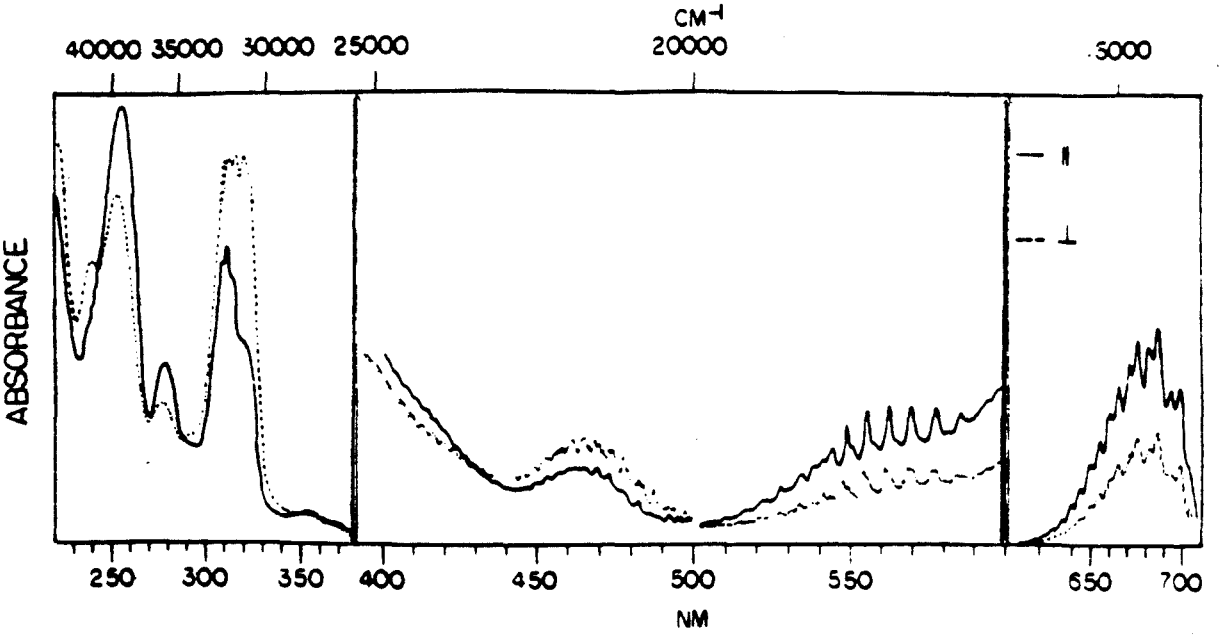
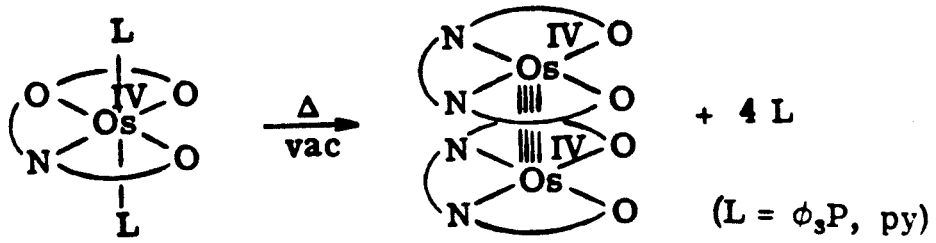


Figure 2.13b. Electronic absorption spectrum of $Re_2Cl_8^{-2}$ at 5°K.

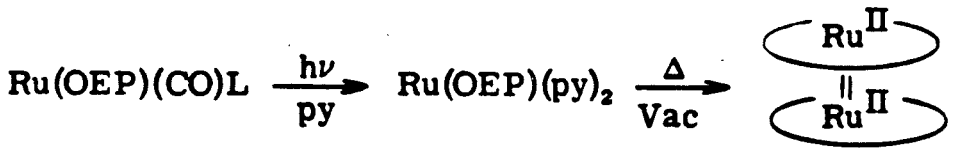
cm^{-1} - 350 cm^{-1}) for metal-metal excited state vibrations (for example, the progression for $Re_2Cl_8^{-2}$ is 248 cm^{-1}).[43]

An experiment that needs to be done is to try to prepare the Os-Os quadruply-bonded dimer independently. A reasonable synthetic method is shown in Equation 2.14a. If the complex, 8,for example, is heated *in vacuo*, it is possible that a multiply-bonded complex will result. This suggestion is based on Collman *et al.*'s synthesis of the Ru(II) porphyrin dimer, shown in Equation 2.14b.[44]

(2.14a)



(2.14b)



18 reacted quickly (within 15 minutes) when CO was bubbled into a methylene chloride suspension to form a bright-purple homogeneous solution. Monitoring the reaction by TLC in methylene chloride showed that one clean compound was present. (A blank reaction without CO did not produce the same results.) An IR spectrum was obtained of the crude reaction mixture that showed what was assigned as a CO stretch at 1980cm^{-1}. The suggested structure, 20, is shown in Scheme 2.6. Unfortunately, after workup, there was no IR peak at 1980cm^{-1}, no ^1H NMR and no meaningful analysis, so the structure cannot really be assigned, merely suggested. The compound appeared to be stable only in the presence of CO. One experiment that needs to be done is to seal 18 in an NMR tube with excess CO and obtain both ^1H and ^{13}C

NMR spectra. It is possible to prepare the compound Os(η^4-HBA-B)(CO)(PPh_3) by bubbling CO through a benzene solution of 8. The IR for this compound has a CO stretch at 1985cm^{-1}.[8]

The biscarbonyl complex, Os(η^4-HBA-B)$(CO)_2$, was highly desirable because it would have provided another possible entrance into bisimido complexes. Condensing biscarbonyl metal complexes with either RNO_2 or RN_3 species produces imido complexes.[3]

An effort to produce a neutral Os(VIII) complex from 18 was made by attempting to oxidize it with elemental sulfur. A number of different reaction conditions were explored and although there was evidence that a reaction of some kind had occurred, no clean products could be isolated. Similarly, unsuccessful attempts were made to produce a neutral dioxo species.

Further Attempts To Prepare a Bisimido Complex

In further efforts to prepare a bisimido complex, other synthetic strategies were explored. Metal-oxo complexes react with phosphinimines to yield imido complexes.[3] The driving force behind this reaction is apparently the formation of the strong P=O bond (130 kcal/mol). The phosphinimine route is a powerful synthetic method, because trimethylsilyl phosphinimine reagent can be facilely prepared from triphenylphosphine and trimethylsilyl azide, and it is easily derivatized to many other phosphinimine reagents. Hydrocarbons will react with trimethylsilyl phosphinimine and exchange an -R group with the $-Si(CH_3)_3$ group. For example, although the synthesis of perfluorophenyl azide is long and arduous, perfluorophenyl phosphinimine can be prepared easily by condensing perfluorobenzene and trimethylsilyl phosphinimine.[34]

Several attempts were made to prepare imido complexes using this method. K_2[Os(η^4-HBA-B)O_2] was stirred with phenyl phosphinimine and trimethylsilyl phosphinimine in two separate attempts. In both cases there was no evident reaction. Another attempt was made using a different ligand system. The monooxo complex, OsO(M_2-Et), was stirred with various

phosphinimine reagents, but there was no evidence of reaction in this case either. No further attempts were made.

Another well-known synthetic method for preparing imido complexes involves the reaction of primary amine compounds with metal oxo complexes. Accordingly, the complex $K_2[Os(\eta^4\text{-HBA-B})O_2]$ was treated with t-butylamine, but no products were isolated. Several other amines were tried with no positive results. This method was also abandoned.

Conclusions

While the major goal of synthesizing a neutral Os(VIII) bisimido compound was not achieved, a number of interesting reactions and compounds were discovered. The first example of a neutral octahedral Os(VIII) compound, formed as an intermediate in the formation of the diimine complex, 9 was postulated. Rather than form a stable Os(VIII) complex, this intermediate underwent an ortho C-H insertion into an aryl ring to form a diimine ligand. In addition, the first example of the formation of a nitrido complex *via* the decompositon of an organic azide was discovered. These two compounds represent rare examples of non-planar amides complexed to transition metals. The synthesis of the monimido complex, 17, is only the second example of an adamantylimido complex. Additionally, there is evidence for the formation of the first osmium-osmium quadruply-bonded complex, 18.

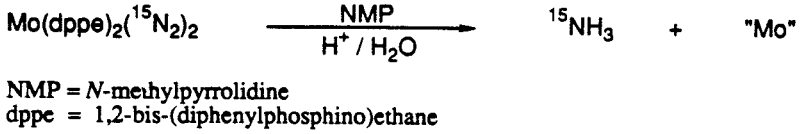
PART ONE: COORDINATION CHEMISTRY OF HIGH-VALENT OSMIUM POLYANIONIC CHELATING LIGAND COMPLEXES WITH IMINE, IMIDO AND NITRIDO LIGANDS

CHAPTER TWO: SECTION II—REACTIONS OF OSMIUM NITRIDO AND METHYLIMIDO COMPLEXES

Introduction

Transition metal nitrido and imido complexes are quite interesting compounds because of their proposed role in catalytic processes related to nitrogen fixation[45], ammoxidation[46] and amination[14] of olefins and possible use as nitrene transfer reagents.[10] Nitrido species have been postulated as intermediates in the reduction of N_2 to NH_3 by molybdenum (see Equation 2.15).[47]

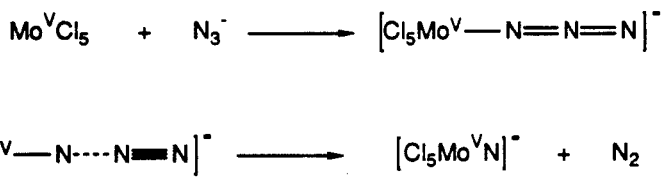
(2.15)



NMP = *N*-methylpyrrolidine
dppe = 1,2-bis-(diphenylphosphino)ethane

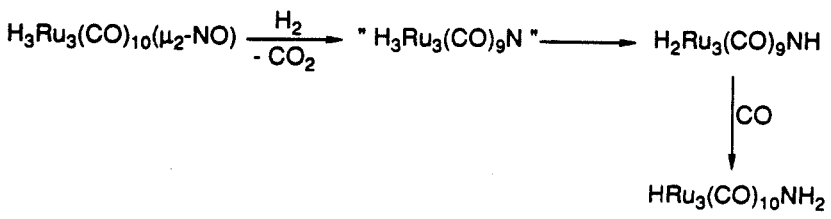
A nitrido intermediate has also been proposed in the fixation of azide to ammonia by molybdenum (see Equation 2.16).[33]

(2.16)



A ruthenium nitrido has also been implicated recently in the reduction of a (μ_2-NO) bridge to (μ_3-NH) and (μ-NH_2) in ruthenium carbonyl clusters (see Equation 2.17).[48]

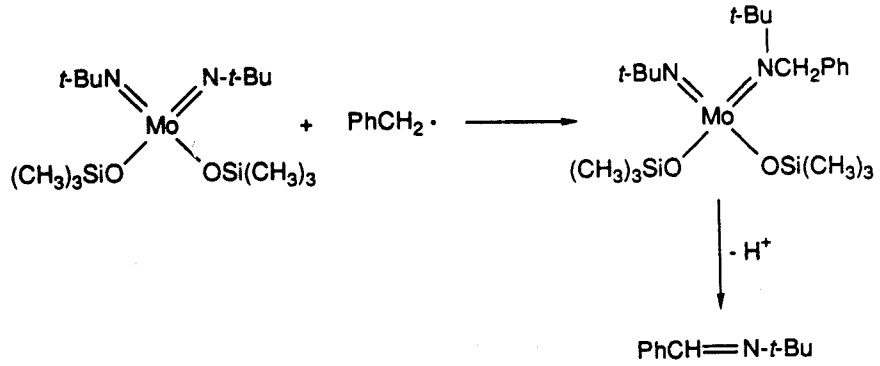
(2.17)



Ammoxidation and amination by imido complexes have been explored both as models for industrial heterogeneous processes and as catalysts in their own right. Sharpless has

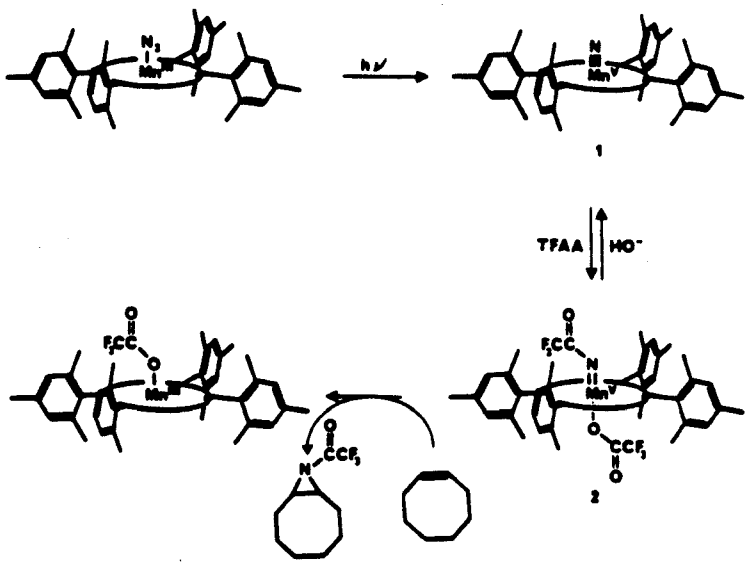
succeeded in the diamination and oxoamination of olefins with bisimidos and oxoimidos (see Scheme 2.1).[14] Chan and Nugent have studied molybdenum imido complexes as models for propylene ammoxidation (see Equation 2.18).[49]

(2.18)



Despite the similarity of nitrenes to carbene species, there has been only one clear example of a nitrido compound's being activated to serve as a nitrene transfer reagent (see Equation 2.19). Groves and Takahashi have succeeded in activating a Mn(V) complex *in situ* and in transferring the imidotrifluoroacetic acid imido moiety to cyclooctene.[50]

(2.19)



The lack of reactivity by nitrido complexes can be partially explained by an examination of the orbital picture. In general, it is believed that nitrido complexes are unreactive as a consequence of the strong π-donation to the metal.[4] Dubois and Hoffmann have performed orbital calculations on five- and six-coordinate ruthenium nitrido complexes.[29] The frontier orbitals are shown in Figure 2.13. For the d^2 systems illustrated, $RuCl_5N^{-2}$ and $RuCl_4N^-$, the orbitals are filled up to the b_2 level. Dubois and Hoffmann propose that the energy of the $2a_1$ orbital (LUMO) is lowered substantially for the 5-coordinate nitrido by distortion of the basal ligands out of the metal plane. Distortion out of the basal plane is caused by the stabilization of the 2e set of orbitals with increasing N-M-L angle. The ligand bending causes increased overlap between the p_z orbitals on nitrogen and the metal d_{xz} and d_{yz} orbitals to form a hybrid orbital (see Figure 2.14). (The four basal ligands are σ-antibonding with respect to Md_z^2. The basal plane distortion moves the ligand orbitals off the d_z^2 torus into a node that drops the $2a_1$ orbital down to a lower energy.)

Figure 2.14. The hybrid orbital formed by the nitrogen p_z orbital and the metal d_{xz} and d_{yz} orbitals.

As a consequence of the low-lying $2a_1$ orbital, Dubois and Hoffmann suggest that the 5-coordinate nitridos will be fairly good electrophiles. The $2a_1$ orbital is approximately 50% nitrogen p_z orbital and 50% metal d_z^2 and may act as an acceptor, either by coordination of a donor ligand to form a 6-coordinate complex (see Equation 2.20)[51] or by reaction at the nitrogen (see Equation 2.21).[52]

(2.20). $NMX_4^- + X^- \longrightarrow MX_5N^{-2}$

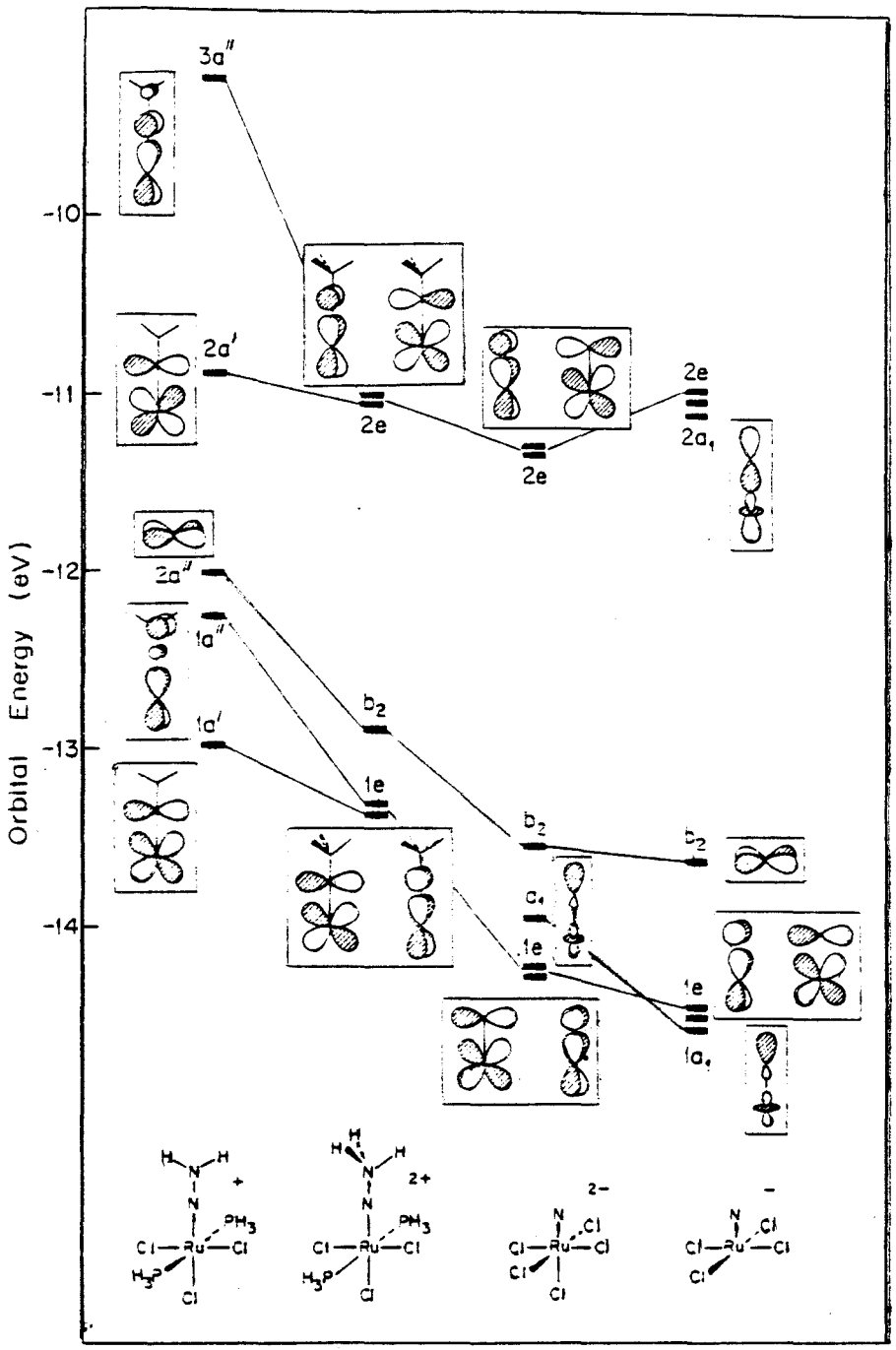
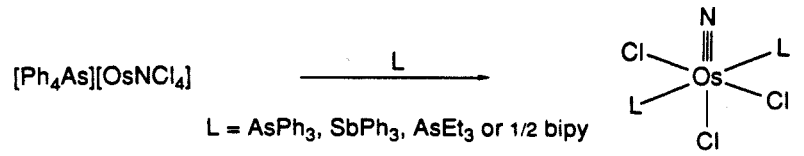


Figure 2.14. The frontier orbitals for five- and six-coordinate ruthenium nitrido complexes.

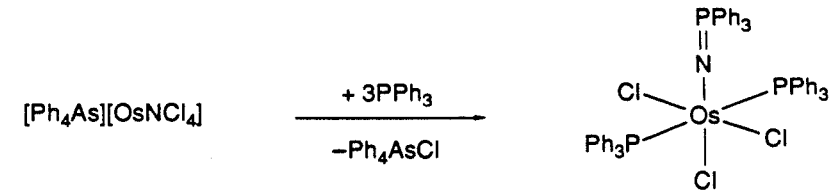
(2.21). $NMX_4^{-2} + PPh_3 \longrightarrow M(NPPh_3)X_4^{-2}$

The observed reactivity does not always bear out the theoretical predictions. Although $OsNCl_4^-$ fails to react with Cl^-, it does react with arsines, stibenes and bipy but does not coordinate the incoming ligand in the axial position (see Equation 2.22).[52] $OsNCl_4^-$ will coordinate PPh_3 at the nitrido to form a phosphine imidate species (see Equation 2.23). It also loses chloride and coordinates triphenylphosphine.[52]

(2.22)

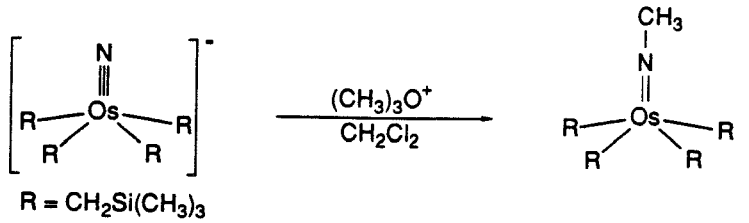


(2.23)



Belmonte has reported the alkylation of a nitrido with RI or $(CH_3)_3O_3^+$ which contrasts with Dubois and Hoffmann's predictions (see Equation 2.24).[28]

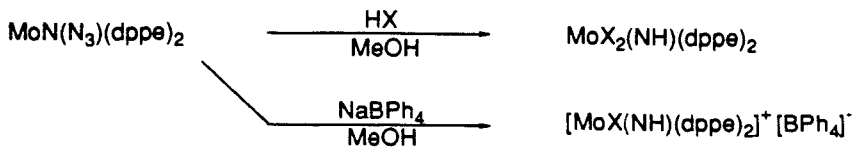
(2.24)



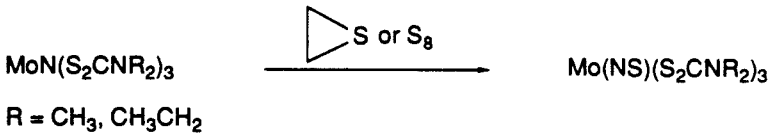
R = $CH_2Si(CH_3)_3$

Coordination of donor ligand in the *trans* axial position changes the electronic environment of the nitrido complex. The orbital picture for $OsNCl_5^{-2}$ indicates that the 6-coordinate nitrido is fairly electron-rich. This is consistent with the observed protonation reaction in an analogous molybdenum compound (see Equation 2.25)[31] and the formation of the thionitrosyl complexes shown in Equations 2.26-2.28.[53]

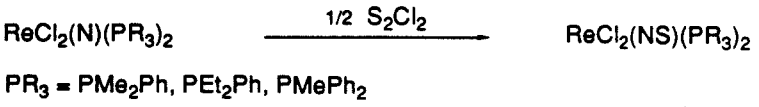
(2.25)



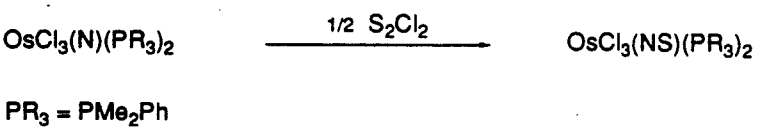
(2.26)



(2.27)



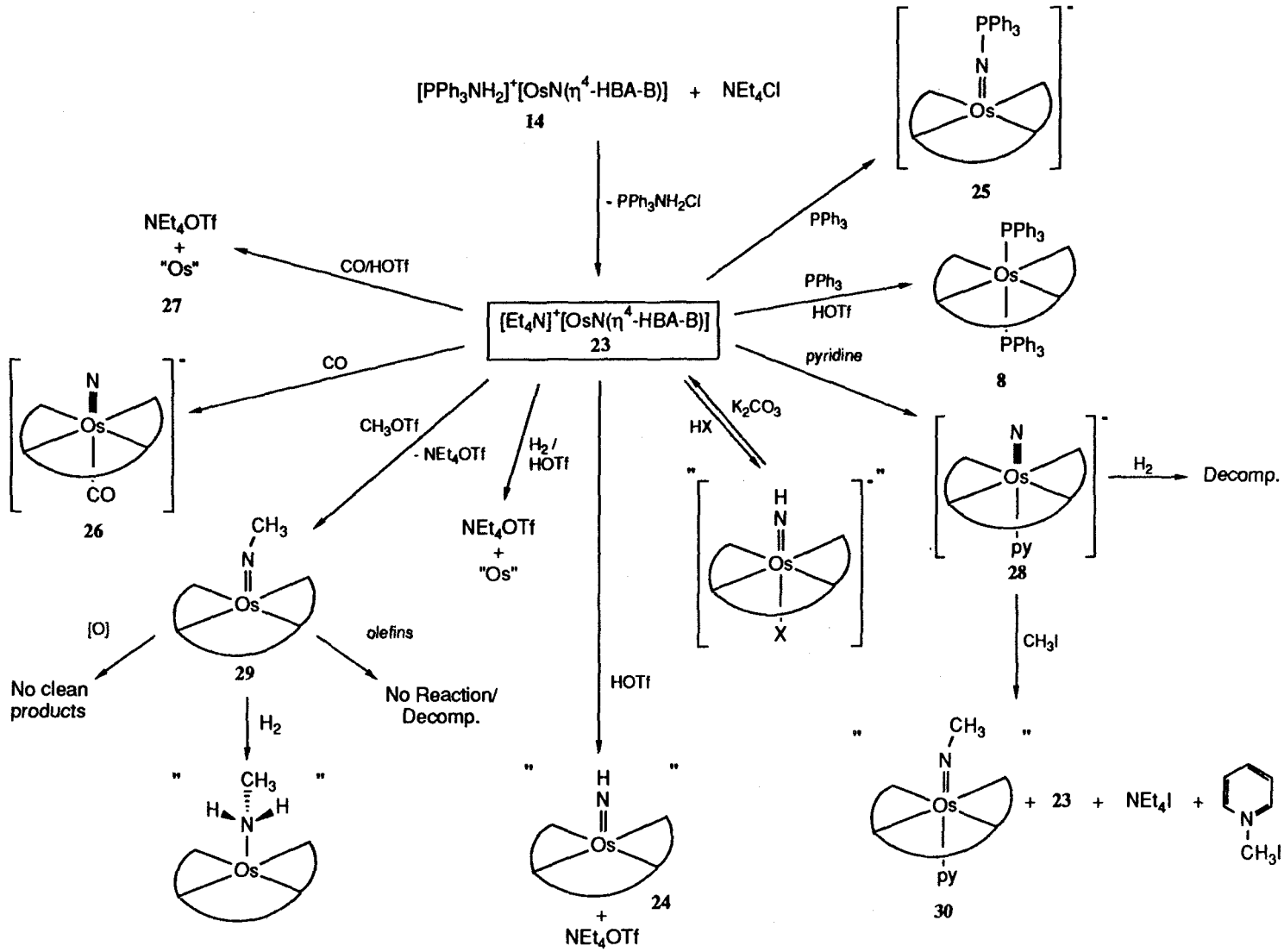
(2.28)



Dubois and Hoffmann's treatment suggests that the osmium nitrido, 14, may be more reactive than other nitridos, considering that it shows a marked distortion. (0.56Å out of the basal plane, *vide supra*). Accordingly, a number of reactions were explored with both electrophilic and nucleophilic reagents.

Results and Discussion

As a preliminary step to studying the reaction chemistry of 14, it was decided to exchange the cation, $[PPh_3{=}NH_2]^+$, for $[NEt_4]^+$, to avoid any unwanted reactions with the cation. 14 was stirred in an acetone/methanol mixture with >1 equivalent of NEt_4Cl for 24 hours (see Scheme 2.7). After rotary evaporation of the solvent, the solid was dissolved in THF from which the yellow mother liquor could be decanted from a white precipitate. The white precipitate was identified as PPh_3NH_2Cl by ^1H and ^{31}P NMR. Very pure $[NEt_4][OsN(\eta^4\text{-(HBA-B)})]$, 23, was collected after preparative TLC (elution with methylene chloride/THF) in 80% yield.



Scheme 2.7. Reaction chemistry of 23.

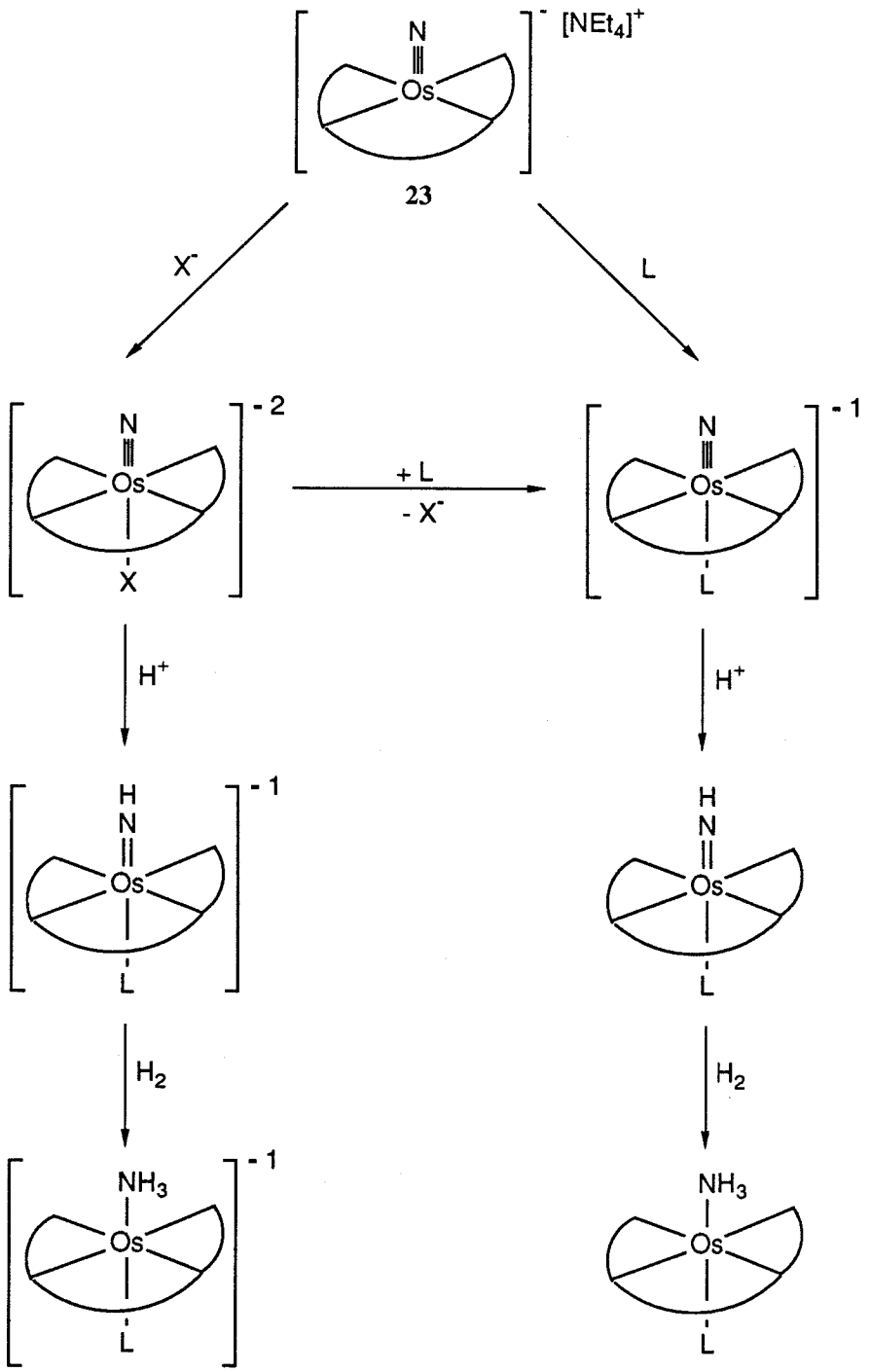
There is always a small amount of 14 recovered from this reaction despite the excess of NEt_4Cl. ^1H NMR showed the expected coordinated PAC ligand peaks, and the IR spectrum showed the Os≡N peak shifted by 53cm^{-1} to 1067cm^{-1}.

In an effort to model the nitrogen fixation work,[45] attempts were made to protonate, hydrogenate and alkylate 23. It was hoped that 23 would be very well behaved and follow an ideal protonation reaction pattern like the one shown in Scheme 2.8. In fact, these reactions proved to be extremely problematic.

When 23 was exposed to mineral acids such as HCl, the solution turned from yellow to pink immediately. This pink compound was very difficult to characterize; however, when a mild base, *i.e.*, K_2CO_3, was added to the pink solution, the solution returned to yellow and the starting compound was recovered quantitatively (see Scheme 2.7).

Addition of one equivalent of triflic acid, (HOTf), at -78° to a methylene chloride solution of 23 produced a cloudy solution from which the white precipitate, identified by ^1H NMR as NEt_4OTf, could be filtered away from the mother liquor (see Scheme 2.7). After preparative TLC (elution with methylene chloride), an ^1H NMR spectrum of the major component showed it to be a single compound, with PAC ligand resonances and a new singlet in the alkyl region (δ1.1), which integrated as 1 proton vs. 12 for the PAC ligand set of peaks. There were no NEt_4 peaks and presumably this is a neutral PAC ligand complex (compound 24, Scheme 2.7.) IR showed no evidence for N-H activity, but the Os≡N band at 1067cm^{-1} disappeared and a new band at 1110cm^{-1} (the Os=N region) appeared. It was not possible to obtain a meaningful microanalysis.

In another effort to protonate the nitrido complex, 23 was heated in a sealed tube of d_6-benzene with one equivalent of HOTf under hydrogen pressure at 110° for two days. The ^1H NMR spectrum showed that the PAC ligand was coordinated and intact, and a new resonance appeared at δ9.7. However, upon workup the only product that could be identified was NEt_4OTf. Similarly, 23 was sealed in a pressure bottle under hydrogen pressure without HOTf. Again, the ^1H NMR spectrum exhibited coordinated PAC ligand peaks, a new resonance at δ9.7



L = some coordinating ligand

Scheme 2.8. Idealized reaction scheme for modeling nitrogen fixation.

and another new peak at δ1.2. Upon workup, no meaningful products other than NEt_4OTf could be isolated in this case either.

On the basis of Dubois and Hoffmann's orbital treatment that 6-coordinate nitrido complexes are fairly electron-rich (*vide supra*), it was hoped that coordination of an axial ligand would facilitate the protonation of 23. It appears, however, that rather than coordination of PPh_3 at an axial site, the preferred site of reaction is at the nitrido moiety. 23 was stirred with PPh_3 in an acetone/methylene chloride mixture with gentle heating. The yellow solution changed to a deep red-brown within .5 hours. A red-brown powder was collected by stirring the reaction mixture in hexanes. An ^1H NMR spectrum showed coordinated PAC ligand, PPh_3 and NEt_4^+ resonances in a 1:1:1 ratio. ^{31}P NMR showed a new peak at δ+37 vs. an internal standard of PPh_3 set at δ-4. The PPh_3 that was added as an internal standard was oxidized to $O{=}PPh_3$ (δ+26). The Os≡N absorption at 1067cm^{-1} disappeared and there a new peak appeared at 1142cm^{-1}, which is in the right range for phosphine imidato osmium complexes (P=N range=1050-1200cm^{-1}).[52] The suggested structure of this complex, 25, is shown in Scheme 2.7. Upon attempting to obtain a purer sample for analysis by preparative TLC, the sample completely decomposed to numerous uncharacterizable compounds. Similarly, the crystals that were sent for crystallographic study decomposed before the data were collected and the x-ray structure obtained was of the decomposition product, $[Na][OsN(\eta^4\text{-HBA-B})]\cdot 2\ O{=}PPh_3$.

There has been only one other report of the preparation of a phosphine imidato osmium complex. Pawson and Griffith prepared a series of $Os(NPR_3)(PR_3)_2X_3$ compounds from $[OsNX_4]^-$ and the appropriate phosphine reagents (see Equation 2.23).[52] They reported that these compounds were quite unstable as well and were unable to obtain any NMR spectra or crystallographic data.

Another attempt was made to protonate 23 in the presence of a coordinating ligand. Accordingly, 23 was treated with HOTf in the presence of triphenylphosphine. There was only a single product that was identified as 8 (see Scheme 2.7).

Similarly, it seemed reasonable to expect that coordination of a CO ligand in the axial site might render the nitrido more susceptible to protonation. A dry THF solution of 23 was heated and CO was slowly bubbled through the solution for several hours (see Scheme 2.7, 26). During the course of this reaction the solution gradually changed from yellow to a rich orange. The THF was removed by rotary evaporation, leaving an orange oil. The IR of this crude material was very similar to 23, with the exception of two additional bands at 1700 and 1775cm^{-1}. The Os≡N band was shifted to 1090cm^{-1}. The ^{1}H NMR spectrum showed the PAC ligand resonances to be shifted slightly upfield from 23. The product decomposed upon being exposed to vacuum, losing the IR bands at >1700cm^{-1}, and was not further characterized. Similarly, when a hot THF solution of 14 was treated with CO over the course of several hours, the solution changed from yellow to orange. The ^{31}P NMR spectrum showed a new resonance at δ+37 (vs. δ+42 for 14). The IR showed bands at 1725 and 1780cm^{-1}, and the nitrido band was shifted to 1072cm^{-1}. ^{1}H NMR spectrum showed the PAC ligand peaks to be shifted slightly upfield. Attempts to crystallize and further characterize this product were also unsuccessful.

When 23 was heated in methylene chloride in the presence of one equivalent of HOTf and CO, the yellow solution slowly (over several hours) turned orange. An IR of the crude reaction mixture was quite similar to that of 26 (see Scheme 2.7). Subsequent isolation of the several products by preparative TLC (elution with CH_2Cl_2/THF) produced a compound that was neutral (*i.e.*, showed no NEt_4^+ peaks), possessed an intact and coordinated PAC ligand, but showed no IR bands >1700cm^{-1} and could not be further characterized (see 27, Scheme 2.7).

Attempts to coordinate an axial ligand to 23 failed either (in the case of triphenylphosphine) because it produced disubstituted complexes or (in the case of CO) because the product was extremely unstable (*vide supra*). It was, however,possible to coordinate a nitrogen donor ligand in the axial site. 23 was heated in a neat solution of pyridine and there was an immediate color change from yellow to orange (see Scheme 2.7). The solution was poured into hexanes and an orange powder was collected. Recrystallization from methylene chloride and hexane yielded yellow crystals. ^{1}H NMR showed coordinated PAC

ligand and pyridine as well as NEt_4^+ resonances. The IR spectrum showed the nitrido peak shifted from $1067cm^{-1}$ to $1080cm^{-1}$. Microanalysis was in excellent agreement with the formulation of the compound as $[NEt_4][OsN(py)(\eta^4\text{-(HBA-B)}]$, 28, (Scheme 2.7).

Contrary to the expectation that a 6-coordinate complex would be more susceptible to protonation, when 28 was treated with HOTf, complete decomposition resulted and no products were isolated.

Only one report of a protonation of a nitrido complex has appeared in the literature.[53] Bishop, Chatt and Dilworth reported the protonation of $MoN(N_3)(dppe)_2$ with concentrated aqueous mineral acids, HX, to give a compound that they identified as $MoX_2(NH)(dppe)_2$ (see Equation 2.25). They failed to find any IR bands assignable to N-H or ^1H NMR peaks attributable to the N-H proton. They also failed to report any Os=N band in the IR. Somewhat more convincing was the reaction of $MoN(N_3)(dppe)_2$ with sodium tetraphenylborate in methanol to give a compound assigned the structure $[Mo(NH)(OMe)(dppe)_2][BPh_4]$ (see Equation 2.25). This compound did show an IR band at $3345cm^{-1}$, but could also be formulated as $[MoN(HOMe)(dppe)_2[BPh_4]$. Belmonte reported that in the case of $[RuN(CH_2SiMe_3)_4]^-$, reaction with HX resulted in the protonation of the M-C bond, while in the case of $OsNR_4^-$, reaction with HX resulted in a new compound $OsNR_2X_2$ (where R= neopentyl).[54] This work however, has yet to appear in the literature.

Fortunately, 23 proved to be more amenable to alkylation than protonation. 23 was stirred at room temperature for 1.5 hours in a methylene chloride solution with one equivalent of methyl triflate (MeOTf) (see Scheme 2.7). The solution slowly turned from yellow to dark-orange. A dark-yellow product was collected after column chromatography (elution with THF/hexane). Yellow-orange crystals were obtained by recrystallization from acetone. ^1H NMR ($DMSO\text{-}d_6$) showed the presence of a coordinated PAC ligand and a resonance at $\delta 4$ that was assigned to the $N\text{-}CH_3$ and an absence of NEt_4^+ resonances. An IR spectrum showed the absence of the nitrido peak at $1067cm^{-1}$ and a new peak at $1105cm^{-1}$ that was assigned as Os=N. The compound was formulated as the neutral complex, 29, (see Scheme 2.7).

Microanalysis was in excellent agreement with this formulation (the presence of 2.5 H_2O molecules was quantified on the analytical sample by ^1H NMR). An attempt was also made to methylate the nitrido with CH_3I. Although NEt_4I was isolated and identified by ^1H NMR, no other product was isolated.

At the time 29 was prepared, it was the first example of a clean methylation of a nitrido compound. Subsequently to this, Belmonte *et al.* reported the successful alkylation of $[NBu_4][OsN(CH_2SiMe_3)_4]$ with Me_3OBF_4 to give $Os(N=Me)(CH_2SiMe_3)_4$ (see Equation 2.4). She also reported the x-ray structure of this compound.[28] In addition, Belmonte reported that the alkylation proceeded smoothly with alkyl iodides, RI, (where R= methyl, ethyl and propyl).[55]

Despite the failure of 28 to protonate, it seemed reasonable to expect that it might be sufficiently activated to allow methylation with a weak methylating agent such as CH_3I. To test this, 28 was stirred in methylene chloride at room temperature with CH_3I .5 hours. The solvent was removed *in vacuo* and the compound was redissolved in THF from which a white solid precipitated. This solid was identified by IR and ^1H NMR as NEt_4I. A yellow solid was collected from the mother liquor after the solvent was removed *in vacuo.* Preparative TLC allowed the collection of several different products. One of the products was identified as 23. Another product was identified as *N*-methylpyridinium iodide by comparison with an independently prepared sample. There was at least one other Os product that could not be further identified, which may be the methylimido pyridine complex 30.

In addition to the protonation and alkylation studies, numerous attempts were made to produce neutral oxidized nitrido species with oxidizing agents, including Br_2, MCPBA, $pyrBr_3$, *t*-butylhydrogen peroxide, hydrogen peroxide and elemental sulfur (see Scheme 2.7). None of these reactions produced clean products, although the nitrido definitely did undergo reactions with a wide variety of reagents.

Reactions of 29

One of the major goals of this project was to prepare imido complexes for use as nitrene transfer reagents on organic substrates. With this in mind, the monoimido complex, 29, produced from the methylation of the nitrido was treated with a number of olefinic substrates.

29 was sealed in NMR tubes with olefins such as styrene, cyclohexene, ethylene and dimethyl fumarate and heated in constant temperature baths at a range of temperatures (60°-110°) for varying lengths of time (.5 hour-2.5 days). Acetone-d_6, benzene-d_6 and chloroform-d_1 were employed as solvents. In all cases there was either no evidence of reaction or the reaction mixture decomposed to a mixture of products from which no meaningful data could be extracted.

An attempt was also made to hydrogenate the methylimido complex. 29 was sealed in an NMR tube under hydrogen pressure and heated in a constant temperature bath (80°-110°) and monitored by ^{1}H NMR for variable reaction times (.5 hour-2 days). Three different solvents were tried: benzene-d6, chloroform-d1, and acetone-d6. In acetone-d6, after .5 hour at 100°, the disappearance of the N-CH3 peak at δ4.2 coincided with the appearance of a new singlet resonance at δ3.3 and a new set of coordinated PAC ligand resonances. Further heating caused decomposition. In benzene-d6 after heating for 2 days at 110°, the disappearance of the N-CH3 resonance at δ4.3 coincided with the appearance of a new triplet resonance at δ3.0 and a new set of coordinated PAC ligand resonances. It may be that these new resonances were due to a coordinated methylamine ligand and that the triplet pattern was only discernible in d6-benzene. In neither case was it possible to assign any N-H resonances. These NMR tube reactions indicate that this line of research is worth pursuing and that 29 may be useful as a model for nitrogen fixation studies.

Numerous attempts were also made to produce either a neutral Os(VIII) compound with oxidizing agents such as MCPBA, TBHP, H_2O_2 and benzoic acid or to coordinate a halogen at

the open axial site with reagents such as pyridinium tribromide, Br_2 and ammonium halides, that might have allowed another path to bisimido complexes. None of these reactions gave clean results.

Conclusions

It has been shown that the nitrido complex, 23, is somewhat more reactive than other nitrido complexes per Hoffmann's predictions, but is more versatile than expected. The nitrido will coordinate a donor ligand at the nitrido site, (PPh_3), and at the axial site (pyridine), and contrary to Hoffmann's expectations, the nitrido complex will also alkylate (and perhaps protonate). The 6-coordinate species, 28, does not appear to be more amenable to alkylation (or protonation) than the 5-coordinate species, 23, at least when the axial ligand is pyridine.

Although the monoimido complex, 29, does not appear to be useful as a nitrene transfer reagent or as a precursor to neutral Os(VIII) or bisimido complexes, it may be a useful model for nitrogen fixation studies.

Experimental

Materials

Acetone, benzene, di-*n*-butylether, diethylether, ethanol, hexanes, methanol, and toluene were reagent grade (Aldrich, Baker, Mallinckrodt, M.C.B. or U.S.I.) and were used as received unless otherwise noted. Methylene chloride and tetrahydrofuran (Baker, Mallinckrodt) were distilled from calcium chloride prior to use. 2-Phenyl azide (10% hydrocarbon solution (P.F.& B), trimethylsilyl azide (P.F. & B.), *p*-toluidine (M.C.B.), dimethyl fumarate (Aldrich), *t*-butylamine (Aldrich), triethylamine (Aldrich), dimethyl malonate (Aldrich), styene (Aldrich), cyclohexene (Aldrich), ethylene (Matheson), *t*-butylpyridine, (Aldrich), pyridine (Aldrich), osmium tetroxide (99.8%, Alfa), potassium carbonate (Mallinckrodt), tetra-*n*-butylammonium chloride (Kodak), methyl iodide (Aldrich), potassium hydroxide, (Baker), hydrogen (Matheson), sodium hydroxide (Baker), triethylamine (M.C.B.), triflic acid (Aldrich), methyl triflate (Aldrich), trifluoroacetic acid (98.5%, M.C.B.), carbon monoxide (Matheson), triphenylphosphine (Aldrich), perfluorophenyl hydrazine (Aldrich), sulfur (Alfa) and sodium nitrite (Aldrich) were all used as received unless otherwise noted. Oxalyl chloride (Aldrich) was freshly distilled before use and o-phenylenediamine (Aldrich) was recrystallized from toluene prior to use. The silica gel used in column chromatography was 60-200 mesh. $K_2Os(OH)_4(O_2)$[16], trimethylsilyl phosphinimine[32] and perflourophenyl azide[37] were prepared according to literature procedure.

Physical Measurements

^{1}H NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer or a Jeol FX90-Q spectrometer, at 270 MHz on a Bruker WM 270 spectrometer, at 400 MHz on a Jeol GX-400 spectrometer, or at 500 MHz on a Bruker WM-500 spectrometer. ^{1}H NMR chemical shifts are reported in ppm(δ) *vs.* tetramethylsilane with the solvent (acetone-d_6) δ2.04, $CDCl_3$ δ7.24, benzene-d_6 δ7.14, CD_2Cl_2 δ5.35, DMSO-d_6 δ2.50) as an internal reference. ^{31}P NMR spectra were recorded at 36.28 MHz on a Jeol FX90-Q spectrometer or on a Bruker WM 270 spectrometer. ^{31}P chemical shifts are reported in ppm(δ) *vs.*an 85% phosphoric acid external standard or an internal standard of PPh_3 set at δ-4. Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Elemental analyses were obtained at the Caltech Microanalytical Laboratory. Electronic spectra were obtained on a Cary 14 spectrophotometer. Raman spectra were attempted on a Spex Ramalog II, at a power of 50 mW- 1 W, irradiating with an argon laser at 488 nm.

X-ray Crystallography Structure Determination of 8

Data collection: The intensity data were collected on a Enraf-Nonius CAD4 diffractometer with Mo Kα radiation and a graphite monochromator (λ0.7107Å) and averaged 4809 reflections.

Unit cell parameters: a=9.26 Å, b=16.03 Å, c=17.88 Å, α=95.4°, β=94.5°, γ=98.7°. The atomic positions of the atoms were derived from the Patterson map. Subsequent Fourier and difference Fourier maps revealed all non-hydrogen atoms. Atomic scattering factors were taken from Stewart, Davidson and Simpson for H, and the International Table for X-ray Crystallograph for all others.

Several cycles of full matrix, least-squares refinement minimizing $\Sigma w(F_o^2-(F_c/k)^2)^2$, $w=\sigma\text{-}2(F_o^2)$, on all non-hydrogen parameters yielded $R=\Sigma ||F_o|-|F_c/k||/|F_o| = 0.091$ and GOF $=\{\Sigma w(F_o^2-(F_c^2/k))^2/n_o-n_p)\}^{1/2} = 1.18$, where n_o was the number of reflections and n_p was the number of parameters; all atomic coordinates were in one block and the scale factor and the isotropic Gaussian ellipsoids were in the other. Calculations were carried out on VAX11/780 and VAX 11/750 computers using the CRYRM crystallographic system.

X-ray Crystallography Structure Determination of 14

Data collection: Oscillation and Weissenberg photographs indicated monoclinic symmetry. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation and graphite monochromator (λ-0.7107 Å) and averaged 5703 reflections.

Unit cell parameters: a=9.56 Å, b=23.68 Å, c=14.38 Å, β=93.26°. The systematic absences led to the assignment of the space group $P2_1/n$ (oko absent for k odd, hol absent for h+1 odd).

The atomic positions of the atoms were derived from the Patterson map. Subsequent Fourier and difference Fourier maps revealed all non-hydrogen atoms. Atomic scattering factors were taken from Stewart, Davidson and Simpson for H, and the International Tables for X-ray Crystallograph for all others.

Several cycles of full matrix least-squares refinement minimizing $\Sigma w(F_o^2 - (F_c/k)^2)^2$, $w=\sigma\text{-}2(F_o^2)$, on all non-hydrogen parameters yielded $R = \{\Sigma||F_o|-|F_c/k||/|F_o|\} = 0.090$ and GOF $= \{\Sigma w(F_o^2 - (F_c^2/k))^2/n_o - n_p)\}^{1/2} = 2.04$, where n_o was the number of reflections and n_p was the number of parameters; all atomic coordinates were in one block and the scale factor and the Gaussian ellipsoids were in the other. Calculations were carried out on VAX11/780 and VAX11/750 computers using the CRYRM crystallographic system.

Syntheses

All reaction were carried out in air unless otherwise noted.

H_4HBA-B, 4,. 2-acetylsalicyclic acid (50.0 g, 0.27 mol) was heated in an excess of oxalyl chloride under a nitrogen atmosphere for 4 hours. Excess oxalyl chloride was removed *in vacuo*. The residue was dissolved in methylene chloride (30 ml) and the methylene chloride removed *in vacuo*. This step was repeated several times. The residue was then dissolved in methylene chloride (100 ml) and chilled in an ice bath. The chilled solution was added drop-wise to a stirred, chilled methylene chloride solution of *o*-phenylenediamine (15.0 g, 0.138 mol). The mixture was stirred 1 hour and an excess of triethylamine was added and stirred another .5 hours. The mixture was treated with 6M NaOH (100 ml) and the organic volatiles were removed on a rotary evaporator. The remaining aqueous solution was decanted from the undissolved organic organic residue. The organic residue was dissolved in a small amount of acetone and treated with a an additional portion of 6M NaOH solution (100 ml). The aqueous solutions were combined and slowly acidified with concentrated HCl. The precipitate was collected, washed with water, and recrystallized from acetone/water. Yield: 78.3 g (81%). Anal. calcd. for $C_{20}H_{16}N_2O_4$: C, 68.98; H, 4.63; N, 8.04. Found: C, 69.04; H, 4.75; N, 8.14. ^{1}H NMR: see Table 2.7.

$[K_2][Os(\eta^4$-HBA-B)$(O_2)]\cdot H_2O$, 7,. A solution of $K_2[Os(OH)_4(O_2)]$ (2.01 g;5.46 mmol) in methanol (500 ml) was added to a solution of 4 (1.9 g; 5.46 mmol) in THF (200 ml) that was continuously stirred. The solution was heated on a hotplate (*ca.* 40°; .5h). After cooling, the clear brown solution was evaporated to dryness on a rotary evaporator. The residue was dissolved in ethanol, di-*n*-butylether was added and the ethanol was removed on a rotary evaporator to give brown crystals. The product was filtered and washed with diethylether. Yield: 3.60 g (100%). Anal. calcd. for $C_{20}H_{12}N_2K_2O_4Os\cdot H_2O$: C, 36.25; H, 2.13; N, 4.23. Found: C, 36.35; H, 2.40; N,4.07. IR (Nujol): 1600 cm^{-1}, νamide; 822 cm^{-1}, νoxo. ^{1}H NMR: see Table 2.7.

Os(η^4-HBA-B)(PPh_3)$_2$, 8,. 7 (1.02 g; 1.58 mmol) and PPh_3 (2.0 g; 6.32 mmol) were dissolved in a mixture of ethanol (25 ml) and THF (45 ml). Excess CF_3CO_2H (.5 ml) was added and the solution was stirred at room temperature (10 min), after which the solution turned from brown to dark-green. Ethanol (20 ml) was added and the solution and the THF was removed on a rotary evaporator to give dark green crystals. The product was filtered and washed with ethanol and hexanes. The solid was recrystallized from dichloromethane/ethanol containing PPh_3 (250 mg). The final product was filtered and washed with ethanol and hexanes. Yield: 1.23 g (73%). Anal. calcd. for $C_{56}H_{42}N_2O_4OsP_2 \cdot .5(H_2O)$, $\cdot .5(CH_3CH_2OH)$: C, 62.74; H, 4.26; N, 2.57. Found: C, 62.67; H, 4.44; N, 2.45. IR (Nujol): 1600 cm^{-1}, νamide. ^1H NMR: see Table 2.7.

Os (η^4-HBA-B)($NHC_6H_4NC_6H_5$), 9,. 600 mg of 8 in 100 ml of benzene in a 250 ml flask fitted with a septum cap were subjected to three freeze-pump-thaw cycles. 2.4 ml (4 eq.) phenyl azide were added *via* syringe. After stirring at room temperature 7-20 days, during which the solution changed from green to brown and finally to purple, the solvent was removed *in vacuo*. A THF/$MeCl_2$ solution of the resultant purple solid was chromatographed on TLC plates by elution with $MeCl_2$. This step was repeated several times. Slow recrystallization from ETOH/hexanes yielded x-ray quality crystals. Yield: 30%. Anal. calcd. for $OsC_{32}H_{22}O_4N_4$: C, 53.62; H, 3.09; N, 7.82. Found: C, 53.49; N, 3.19; N, 7.65. IR (Nujol): 1650, 1600 cm^{-1}, νamide. ^1H NMR: see Table 2.7.

[PPh_3=NH_2][OsN(η^4-HBA-B)], 14. 100 mg of 8 in 50 ml of degassed benzene in a 150 ml flask fitted with a septum cap were subjected to three freeze-pump-thaw cycles. Under a nitrogen blanket, 0.022ml (2 eq.) of Me_3SiN_3 were added *via* syringe. The solution was allowed to stir at room temperature overnight, during which it changed from green to pale yellow and a precipitate fell from solution. The yellow precipitate was filtered and washed with hexanes. Recrystallization from $MeCl_2$ yielded large x-ray quality crystals. Yield: 80%. Anal. calcd. for.$OsC_{38}H_{29}O_4N_4P$: C, 55.20; H, 3.53; N, 6.78. Found: C, 55.01; H, 3.67; N, 6.44. IR (Nujol), 1637 cm^{-1}, νamide; 1120 cm^{-1}, νOs=N. ^1H NMR: see Table 2.7.

Os (N-$C_{10}H_{16}$)(η^4-HBA-B)(PPh_3), 17. A benzene solution of 500 mg of 8 was subjected to three freeze-pump-thaw cycles and 738 mg of 1-adamantyl azide in benzene were added *via* syringe. The solution was allowed to stir at room temperature for 1 day during which the solution changed from green to a rich brown. The solvent was removed *in vacuo* and a brown powder was collected and washed with hexanes. The brown powder was purified by preparative TLC by elution with 3:1 $MeCl_2$/acetone and collected in 60% yield. Successive TLC steps were necessary to obtain a pure product at 10% overall yield. Anal. calcd. for $OsC_{48}H_{43}O_4N_3P$: C, 60.94; H, 4.48; N, 4.44. Found: C, 61.36; H, 4.92, N, 4.90. IR (Nujol): 1602 cm^{-1}, νamide; 1180 cm^{-1} , νOs=N. ^1H NMR: see Table 2.7.

[Os(η^4HBA-B)]$_2$, 18. To a degassed benzene solution of 2 g of 8, 2 ml of perfluorophenyl azide were added *via* syringe. The solution was stirred at room temperature for 2 hours, during which the green solution became black. The reaction was monitored by TLC and allowed to continue until the starting material had all disappeared. The solvent was removed on a rotary evaporator and dried *in vacuo*. The black residue was insoluble in all solvents with the exception of hot DMSO and could not be mulled for an IR spectrum. No ^1H or ^{19}F NMR spectra could be recorded of the black residue. Anal. calcd. for $Os_2C_{40}H_{24}O_8N_4$: C, 44.94; H, 2.26; N, 5.24. Found: C, 44.94; H, 2.93; N, 4.39.

[Os(η^4-HBA-B)(DMSO)]$_2$•2H_2O, 19. 18 was dissolved in hot DMSO and allowed to cool slowly. Black crystals were collected and dried *in vacuo.* Anal. calcd. for $Os_2C_{44}H_{40}O_{12}N_4S_2$: C, 41.90; H, 3.20; N, 4.44. Found: C, 41.95; H, 2.91; N, 4.43. IR (Nujol): 1650, 1602 cm^{-1}, νamide; 925, 940 cm^{-1}, νO-bound DMSO. ^1H NMR: see Table 2.7.

"[Os(η^4-HBA-B)(CO)]$_2$", 20. CO gas was slowly bubbled through a suspension of 50 mg of 18. Over the course of three hours, the solution changed from a black suspension to a brilliant-purple homogeneous solution. The reaction was monitored by TLC (elution with $MeCl_2$) and was complete after three hours. TLC showed the presence of a single, purple compound. The solvent was removed on a rotary evaporator. Further workup involved drying the purple

compound *in vacuo*, which apparently pumped away the CO ligands. No analytical or ^{1}H NMR data were obtained. IR (Nujol) on crude purple material: 1695, 1635 cm^{-1}, νamide; 1980 cm^{-1}, νM-CO.

[Os(η^4-HBA-B)(*t*-Bupy)$_x$(solvent)$_{2-x}$]$_2$ (x=2 or 1), 21 or 22. 75 mg of 18 were allowed to stir in a benzene suspension with an excess of *t*-butylpyridine. The solution slowly changed from black to brown over the course of several hours. The solvent and excess *t*-butylpyridine were removed *in vacuo*. Attempts were made to recrystalize the residue from DMSO and other solvents. Anal. calcd. for $Os_2C_{58}H_{50}O_8N_6$: C, 52.01; H, 3.76; N, 6.27. Found: C, 52.71; H, 4.27; N, 5.57.

[NEt$_4$][OsN(η^4-HBA-B)], 23. 700 mg of 14 were stirred in a acetone/MeOH solution with 250 mg (2 eq.) of NEt_4Cl at room temperature for 24 hours. The solvents were removed on a rotary evaporator and the yellow residue was dried *in vacuo*. The solid was redisolved in THF from which a white solid (PPh_3=NH_2Cl) precipitated. The yellow mother liquor was decanted away from the solid and dried *in vacuo*. Pure 23 was obtained by preparative TLC by elution with $MeCl_2$/THF in 80% yield. IR (Nujol): 1600, 1619 cm^{-1}, νamide; 1067 cm^{-1}, νOs=N. ^{1}H NMR: see Table 2.7.

"Os(NH)(η^4-HBA-B)", 24. A degassed $MeCl_2$ solution of 23 was cooled to -78° and one equivalent of HOTf was added *via* syringe. The solution was allowed to warm to room temperature, and a white precipitate fell out of solution immediately. The yellow mother liquor was decanted away from the solid and rinsed with $MeCl_2$ and THF. The solvent was removed *in vacuo*, leaving a yellow residue. The white precipitate was identified as NEtOTf by ^{1}H NMR. The yellow solid was purified by preparative TLC by elution with THF/$MeCl_2$. Only the major fraction (R_f=1) was collected. No analytical data were obtained. IR (Nujol): 1620, 1600 cm^{-1}, νamide; 1120 cm^{-1}, νOs=N. ^{1}H NMR: see Table 2.7.

$NEt_4Os(N{=}PPh_3)(\eta^4$-HBA-B), 25. An acetone solution of 300 mg of 23 was gently heated on a hot plate (*ca.* 45°) for .5 hour, during which the solution changed from yellow to red-brown. TLC (elution with THF/$MeCl_2$) showed there to be several products. The solution was poured into hexane and the resultant brown powder was collected by filtration. Preparative TLC (elution with acetone/$MeCl_2$) allowed the collection of the major product (R_f= .7) in 60% yield. This step was repeated several times with an overall yield of about 30%. Anal. calcd. for $OsC_{46}H_{47}N_4O_4P$: C, 58.71; H, 5.03; N, 5.95. Found: C, 52.65; H, 3.52; N, 4.58. IR (Nujol): 1601, 1617 cm^{-1}, νamide; 1142 cm^{-1}, νP=N. ^{31}P NMR: δ+37 (s), *vs.* δ-4 (PPh_3). ^1H NMR: see Table 2.7. The powder was recrystallized from acetone which afforded x-ray quality crystals for which the structure was analyzed as $NaOsN(\eta^4$-HBA-B) •2 $O{=}PPh_3$. It was subsequently determined by ^{31}P NMR that PPh_3 was oxidized spontaneously to $O{=}PPh_3$ by 25.

"$NEt_4OsN(\eta^4$HBA-B)(CO)", 26. CO was allowed to bubble slowly through a dry THF solution of 411 mg of 23 for several hours at room temperature as the solution slowly changed from yellow to orange. The solvent was removed on a rotary evaporator, leaving an orange oil. IR (Nujol): 1600, 1615 cm^{-1}, νamide; 1765, 1700, νCO(?); 1090 cm^{-1}, νOs=N. Further workup procedure, including *in vacuo* drying, resulted in the loss of the IR bands at >1700, and the compound was not further characterized.

[NEt_4][$OsN(\eta^4$-HBA-B)(py)], 28. 400 mg of 23 were stirred in neat pyridine and gently heated on a hot plate (*ca.* 40°). There was an immediate color change from yellow to deep-orange. The reaction solution was poured into hexanes and a brown-orange powder was collected. The solid was filtered and washed with hexanes and recrystallized from $MeCl_2$ and hexane. Yellow crystals were obtained in 60% yield. Anal. calcd. for $OsC_{33}H_{37}O_4N_5$: C, 52.30; H, 4.92; N, 9.24. Found: C, 52.12; H, 5.03; N, 8.96. IR (Nujol): 1602, 1590 cm^{-1}, νamide; 1180 cm^{-1}, νOs=N. ^1H NMR: see Table 2.7.

$Os(NCH_3)(\eta^4$-HBA-B), 29. To a dry $MeCl_2$ solution of 300 mg of 23, 44 μl (1 eq.) MeOTf were added *via* syringe and allowed to stir at room temperature for 1.5 hours. The solution turned

from yellow to orange and would turn brown if left for longer periods of time. The solvent was removed *in vacuo*, the residue was redissolved in THF and subsequently column-chromatographed by elution with THF/hexanes. An orange solid was isolated as the major product in 80% yield. Yellow-orange crystals were obtained from acetone. Anal. calcd. for $OsC_{21}H_{15}O_4N_3$: C, 44.76; H, 2.68; N, 7.46. Found: C, 44.27; H, 2.73, N, 7.27. IR (Nujol): 1600, 1635 cm^{-1}, νamide; 1105 cm^{-1}, νOs=N. ^1H NMR: see Table 2.7.

[NEt_4][OsN(η^4-HBA-B)(py)], 30. 100 mg of 28 were stirred in neat MeI at room temperature. After .5 hour, a yellow precipitate was formed. The solvent was removed *in vacuo* and the residue was analyzed by TLC (elution with THF), which showed the presence of several products. The residue was dissolved in THF from which a white powder was collected and identified by ^1H NMR as NEt_4I. Preparative TLC under the same conditions allowed the collection of three products. One of the products was identified as 23. One of the other products was identified as *N*-methylpyridinium iodide by comparison with an independently prepared sample. No other products were completely identified.

Table 2.7. ^1H NMR data

Compound	Solvent	PAC Ligand	Ligand
4	acetone-d_6	7.6-8.0 (m, 4H)	
		7.2-7.5 (m, 4H)	
		6.7-7.0 (m, 4H)	
7	acetone-d_6	6.4-6.9 (m, 8H)	
		8.3 (dd, 2H)	
		9.1 (dd, 2H)	
8	$CDCl_3$	-4.33 (dd, 2H)	(PPh_3)
		-3.95 (dd, 2H)	8.28 (d, 12H)
		1.33 (d, 2H)	6.99 (t, 12H)
		4.27 (dd, 2H)	7.36 (t, 6H)
		6.99 (m, 2H)	
		8.19 (m, 2H)	
9	$CDCl_3$	8.34 (d, 2H)	($NHC_6H_4NC_6H_5$)
		8.05 (d, 2H)	6.9 (d, 1H)
		7.3 (m, 2H)	6.45 (t, 1H)
		7.05 (m, 4H)	6.36 (d, 1H)
		6.83 (t, 2H)	6.24 (d, 1H)
			7.05 (m, 3H)
			11.65 (b, 1H)

Compound	Solvent	PAC Ligand	Ligand
14	acetone-d_6	9.0 (dd, 2H)	(PPh_3)
		8.28 (dd, 2H)	7.26 (m, 15H)
		6.87-7.23 (m, 8H)	
17	acetone-d_6	(PAC + PPh_3)	(N-$C_{10}H_{16}$)
		9.11 (d, 2H)	1.79 (m, 16H)
		8.80 (d)	
		8.25-8.18 (m)	
		7.41 (m)	
		6.96 (m) } = 25 H	
19		8.05 (m)	(DMSO)
		7.5 (m)	2.5 (b, 12H)
		7.02 (m)	(H_2O)
		6.55 (m) } = 12H	2.87 (b, 4H)
21	$CDCl_3$	(PAC + *t*-Bupy)	(DMSO)
		7.3 (d, 2H)	2.5 (b,12H)
		6.5 (t)	(*t*-Bupy)
		6.2 (m)	2.05 (s, 4.5H)
		5.6 (m)	
		4.9 (dd)	
		1.8 (d)	
		1.2 (m)	
		.95 (m) } = 15H	

Compound	Solvent	PAC Ligand	Ligand
23	acetone-d_6	9.15 (dd, 2H)	(NEt_4^+)
		8.3 (dd, 2H)	3.15 (q, 8H)
		7.6 (m, 8H)	1.2 (td, 12H)
24	DMSO-d_6	8.94 (dd, 2H)	(N-H) ?
		8.15 (dd, 2H)	4.9 (b, 2H)
		7.0 (m, 8H)	
	acetone-d_6	9.1 (dd, 2H)	1.2 (s, 1H)
		8.2 (dd, 2H)	
		7.1 (m, 8H)	
25	acetone-d_6	(PAC + PPh_3)	(NEt_4^+)
		9.12 (dd, 2H)	3.4 (q, 8H)
		8.27 (dd, 2H)	1.2 (td, 12H)
		6.86-7.91 (m, 23H)	
28	acetone-d_6	(PAC + py)	(NEt_4^+)
		9.1 (dd, 2H)	3.15 (q, 8H)
		8.45 (m)	1.12 (td, 12H)
		8.25 (dd)	
		7.65 (m)	
		7.0 (m) } = 15 H	
29	acetone-d_6	9.16 (dd, 2H)	($N-CH_3$)
		8.28 (dd, 2H)	4.3 (s, 3H)
		7.27 (m, 8H)	

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PART II: ASYMMETRIC HYDROGENATION USING A RESOLVED CHIRAL SCANDIUM HYDRIDE COMPLEX

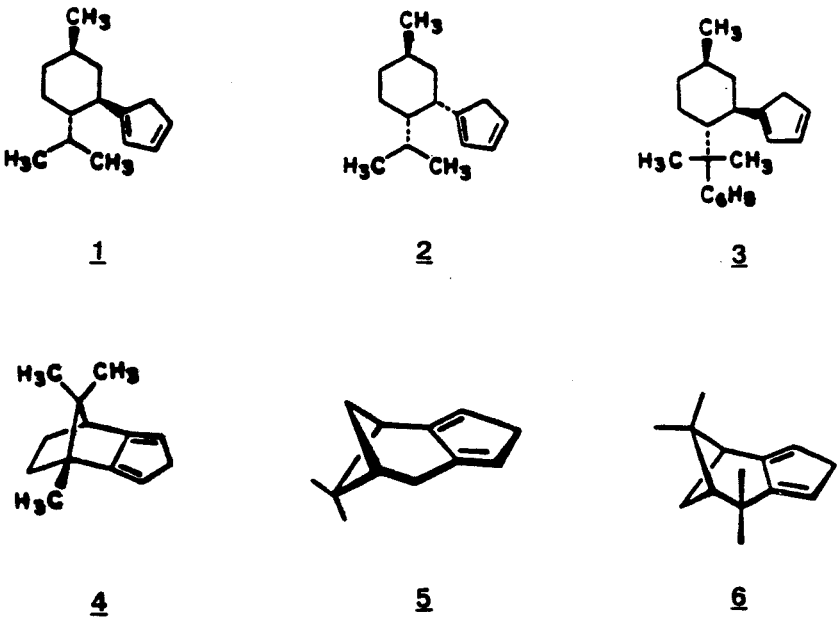
CHAPTER ONE: INTRODUCTION

Introduction

Asymmetric synthesis has been an active research area and a field full of challenge for the chemist since the discovery of stereoisomerism in the late 19th century.[1] Amino acids, carbohydrates and nucleotides all exist in nature in predominantly one enantiomeric form.[1] Despite the prevalence of chiral compounds and their recognized importance, it was not until the advent of asymmetric hydrogenation in the mid-1950's that chemists began to be able to produce enantiomerically pure compounds catalytically without enzymes.[2] Transition metal complexes have played a major role in the development of asymmetric hydrogenation catalysts.[2] Early synthetic approaches produced compounds that catalyzed asymmetric reactions that achieved only modest enantiomeric excesses (e.e.) of 10-15%.[2] Since that time a great deal of research effort has been devoted to this area and a degree of sophistication has been achieved; for example, chiral organic transformations mediated by transition metal complexes have been incorporated into the total synthesis of complex natural products.[3] An advantage of using transition metal complexes for asymmetric synthesis is that the reactions can be "tuned" by varying the ligand environment of the metal, making it possible to produce different catalysts for specific substrate reactions. The greater part of the work in this area has been with chiral phosphine ligands, a field that was opened up by two simultaneous events: the discovery of a rhodium hydrogenation catalyst by Wilkinson in 1965,[3] and the development of a method to synthesize a wide variety of chiral phosphines by Mislow.[4] These discoveries led to the synthesis of hundreds of chiral phosphine complexes of rhodium or other metals for use as asymmetric hydrogenation catalysts and in other asymmetric reactions .[5] Although the chiral phosphine complexes have achieved success as asymmetric catalysts, there are some disadvantages associated with using chiral phosphines as ligands. In order for the efficient transfer of asymmetry to the substrate to occur, the chiral ligands must remain bound to the metal during the stereodifferentiating step; phosphine ligands have traditionally been

recognized as being quite labile.[6] In an effort to prepare more robust asymmetric catalysts, new chiral ligand types have been sought.[7]

One approach that has been taken involves incorporating chirality into common transition metal ligands such as the cyclopentadienyl (Cp) moiety.[7] Cp ligands offer at least one advantage over phosphine ligands in that they form strong η^5-bonds to the metal. Another advantage is that chirality can be incorporated into Cp ligands, using cheap and readily available natural products from the "chiral pool." Chiral Cp menthyl, neomenthyl (Cp^{men},1, Cp^{nmen},2),[9,10,11,12] and phenylmenthyl (Cp^{pmen},3)[6], Cp camphor(Cp^{cam},4)[6,13], Cp pinene (Cp^{pin},5)[13] and Cp verbenone (Cp^{ver},6)[14] (see Figure 1.1) complexes have been prepared with titanium, iron or ruthenium.



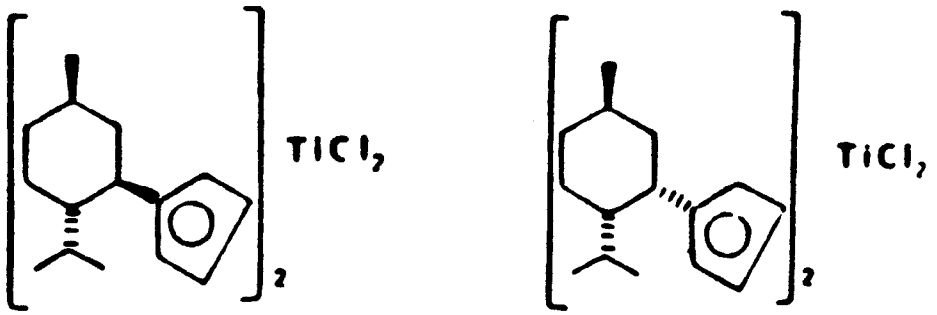
1 2 3

4 5 6

Figure 1.1. Chiral Cp ligands.

Several of the chiral Cp complexes have proved to be active asymmetric hydrogenation catalysts. For example, Cesarotti *et. al.* reported that (Cp^{men} or Cp^{nmen})$_2TiCl_2$, 7, and 8, (see Figure 1.2) will hydrogenate 2-phenyl-1-butene to 2-phenylbutane in the presence of a

cocatalyst, $LiAlH_2(OR)_2$, with a modest e.e. ranging from 1-28% (see Table 1.1). These catalysts do not appear to be very general, as the other prochiral olefins tested, α-ethoxy and α-methoxystyrene, were not hydrogenated.[11]



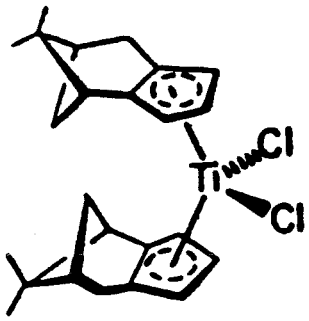
7 8

Figure 1.2. Chiral Cp^{men} or Cp^{nmen} catalysts.

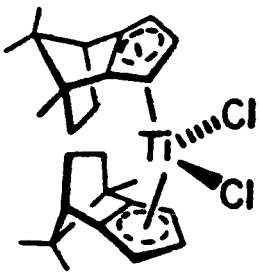
Catalyst	Temp. (°C)	O.Y. and abs. conf. of 2-phenylbutane			
		$LiAlH_2(OCH_2CH_2OCH_3)_2$		$LiAlH_2(OtBut)_2$	
7	−5	22	(*S*)-(+)		
	+5	28	(*S*)-(+)		
	+20	15	(*S*)-(+)	15	(*S*)-(+)
	+30	16	(*S*)-(+)	16	(*S*)-(+)
	+40	10	(*S*)-(+)	11	(*S*)-(+)
8	+20	7	(*R*)-(−)		

Table 1.1. Data for the asymmetric hydrogenation of 2-phenyl-1-butene.

Paquette *et al.* have reported that $(Cp^{pin})_2Ti\ Cl_2$, 9, or $(Cp^{cam})_2TiCl_2$, 10, (see Figure 1.3) will hydrogenate α-ethylstyrene or 2-ethyl-1-hexene to 2-phenylbutane or 3-methylheptane, repectively, in the presence of *n*-butyllithium or $LiAlH_2(OCH_2CH_2OCH_3)_2$, with an e.e. ranging from 0.1-34% (see Table 1.2).[13]

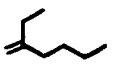
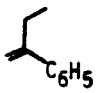


9



10

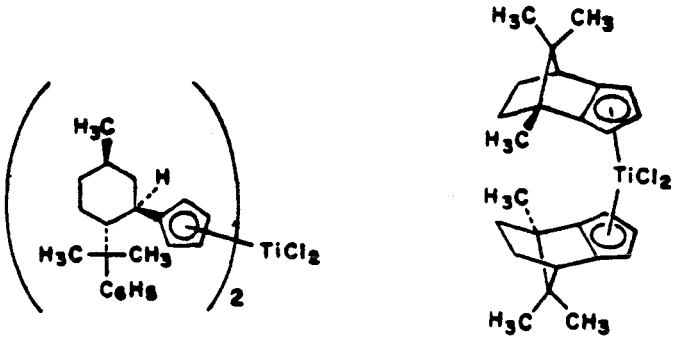
Figure 1.3. Chiral $(Cp^{pin})_2TiCl_2$ and $(Cp^{cam})_2Ti_2$ catalysts.

Complex	Temp	Method of activation	% enantiomeric excess (abs. config.)	
				
9	20°C	Red-Al	0.1 (R)	1.7 (S)
	20°C	n-BuLi	---	2 (S)
	-20°C	n-BuLi	---	6.9 (S)
10	20°C	Red-Al	2.2 (S)	14.1 (R)
	0°C	Red-Al	---	23.7 (R)
	-20°	n-BuLi[b]	---	34

Red-Al = $LiAlH_4(OCH_2CH_2OCH_3)_2$

Table 1.2. Data for the asymmetric hydrogenation of α-ethylstyrene and 2-ethyl-1-hexene.

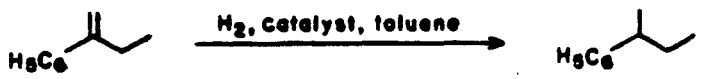
Vollhardt *et al.* have achieved a higher e.e. for the hydrogenation of α-ethylstyrene to 3-methylheptane using the catalysts $(Cp^{pmen})_2TiCl_2$, 11, or $(Cp^{cam})_2TiCl_2$, 12, in the presence of *n*-butyllithium or $LiAlH_2(OCH_2CH_2OCH_3)_2$ (see Figure 1.4).[6]



11 12

Figure 1.4. Chiral Cp^{pmen} or Cp^{cam} catalysts.

The optical yields* reported were between 22 and 34%, the highest yet achieved for the asymmetric hydrogenation of simple unfunctionalized olefins (see Table 1.3).[6]



cat. precursor	inductn time	temp, °C	time	optical yield, %
11	1 h	20	40 h	33
	2 min	20	20 min	22
	2 min	0	40 min	25
12	2 min	-20	5 h	34

Table 1.3. Data for the asymmetric hydrogenation of α-ethylstyrene.

*Note: Optical yield, optical purity and enantiomeic excess (e.e.) are commonly used synonymously; however, the term e.e. is defined as %R-%S = e.e.% and is more correct for determinations made by NMR; optical purity (o.p.) is defined as o.p. = $[\alpha]/[\alpha_{max}] \cdot 100\%$ and is more correct for determinations made by polarimetry.[1,3,5,7] The terms are used here as the original authors reported them.

While these reactions mark the beginning of a fruitful area of research in asymmetric hydrogenation catalysts prepared with chiral Cp ligands for simple olefins, there is much room for new developments. The stereoselectivity that has been achieved so far, while improving, is still not in the range that would make these catalysts useful for commercial processes. Reported here are further efforts to prepare a useful catalyst. The main goal of this research project was to prepare a resolved chiral Cp scandium hydride complex and to explore its capability in asymmetric hydrogenation of an unfunctionalized olefin.

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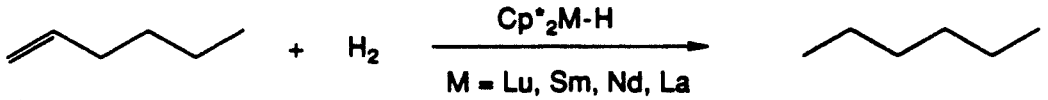
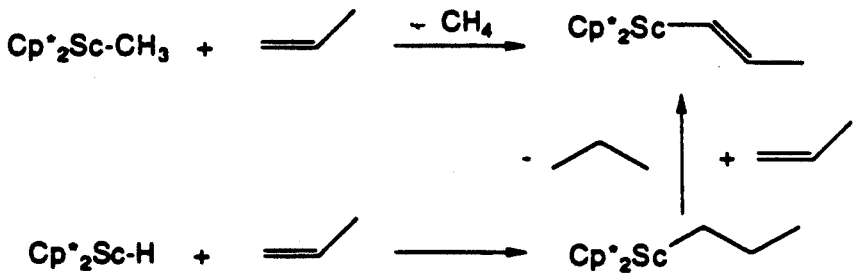
CHAPTER TWO: ASYMMETRIC HYDROGENATION WITH

$(Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3(1R,2R,5S)\text{-menthyl})SCH.$

Introduction

Permethylmetallocene complexes of lanthanides and group 3 metals of the general formula $(Cp^*)_2MH$ (where M = Sc, La ,Sm, Lu or Nd and Cp^* = (η^5-C_5Me_5)) have been shown to function as hydrogenation catalysts for simple olefins (see Equations 2.1 and 2.2).[1,2]

(2.1) 

(2.2) 

The scope of reactivity of these compounds has been somewhat limited by the steric constraints imposed by the large Cp^* ligands. In an effort to reduce steric bulk, a new class of Cp ligands was synthesized with a dimethylsilylene bridge linking the two Cp ligands.[3] This approach was successful in producing a smaller ring centroid-metal-centroid ring angle (the angle is smaller by 14.7° relative to $Cp^*_2ScCH_3$) and in opening up a "wedge" of reactivity in the coordination sphere of the metal.[2,4] This structure was established by an x-ray diffraction study (see Figure 2.1).[4]

Several $SiMe_2$-bridged Cp_2 derivative ligands have been prepared and complexed to scandium, and the chemistry has been extensively explored.[4] It has been demonstrated that two of these complexes, $Me_2Si(\eta^5\text{-}C_5Me_4)_2Sc(H)(PMe_3)$ (OpScH(PMe_3)), and (*meso*-$Me_2Si(\eta^5$-*t*-butyl$C_5H_3)_2(H))_2$ ((DpScH)$_2$), will promote the catalytic dimerization of α-olefins and the catalytic cyclization of α,ω-diolefins. When the cyclization of α-ω reactions is performed in the presence of hydrogen, the final products are hydrogenated (see Scheme 2.1.).[4]

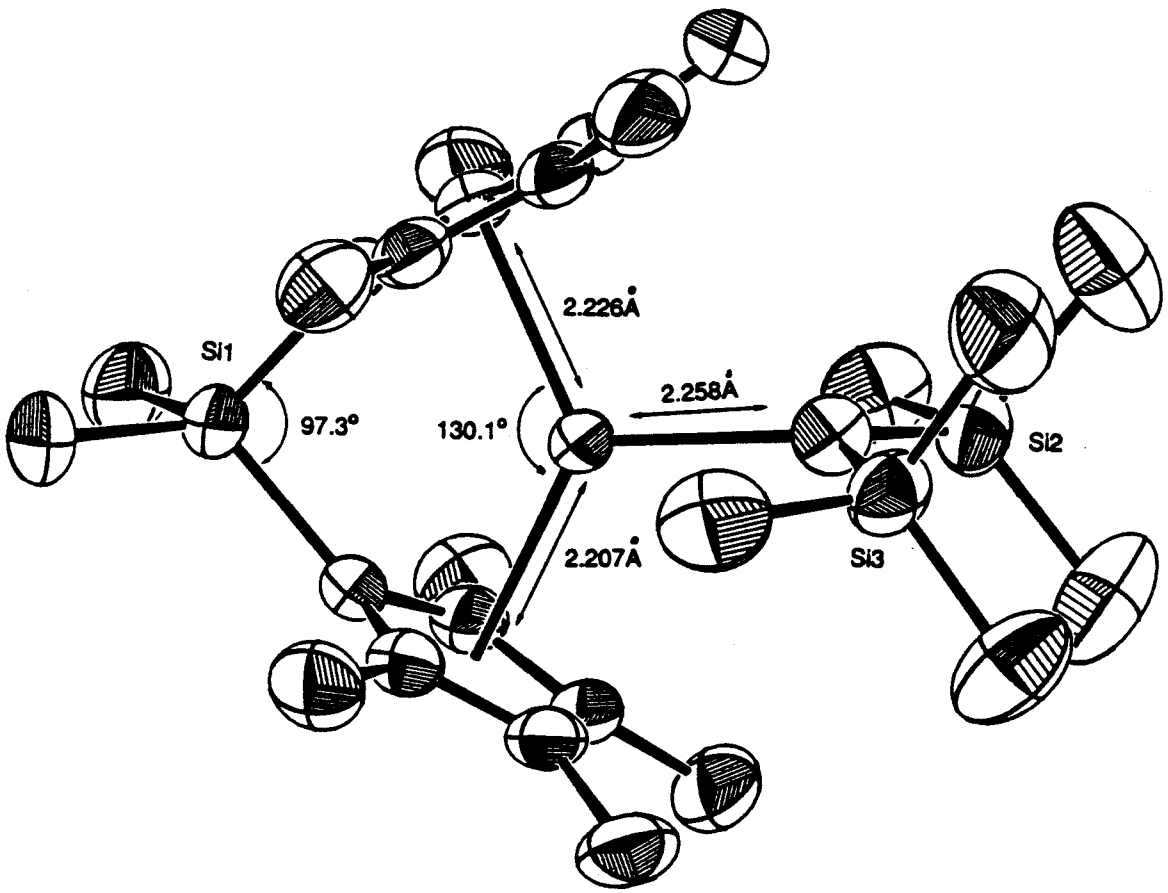
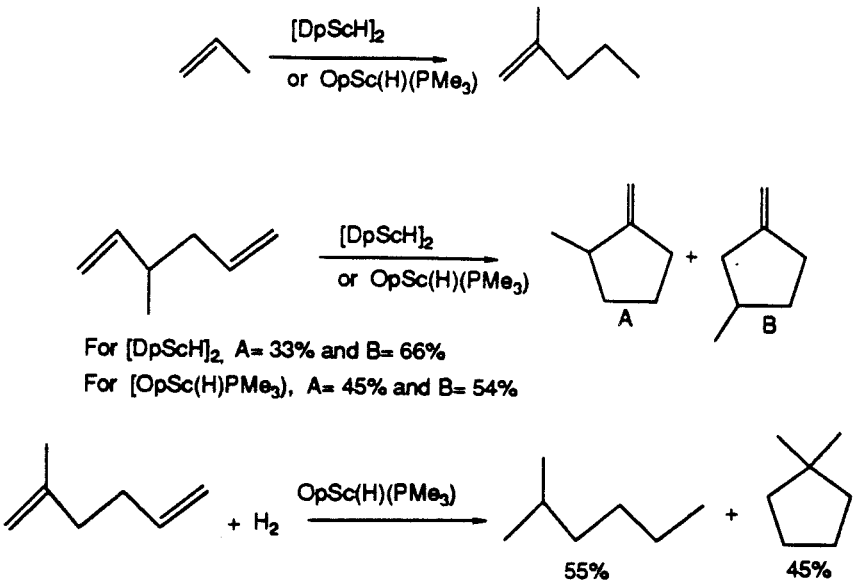


Figure 2.1. The molecular structure of $(Me_2Si(\eta^5\text{-}C_5Me_5)_2)ScCH(SiMe_3)_2$ showing the open "wedge."



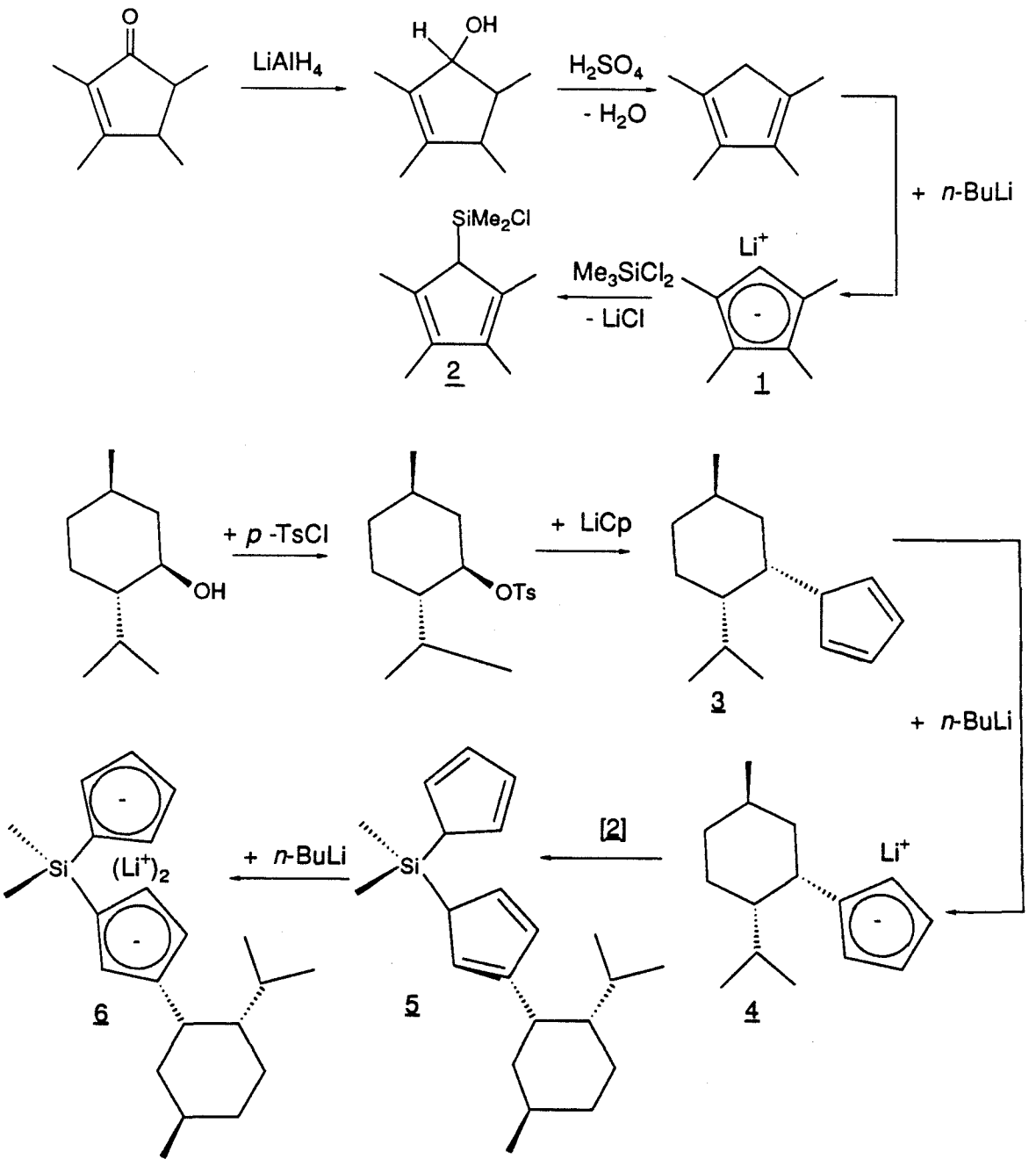
Scheme 2.1. $(DpScH)_2$ and $OpScH(PMe_3)$ will dimerize, and cyclize α-olefins and α,ω-olefins, respectively.

It is the purpose of the present work to show that it is possible to extend this reactivity to include the asymmetric hydrogenation of a prochiral olefinic substrate by incorporating chirality into one of the Cp ligands.

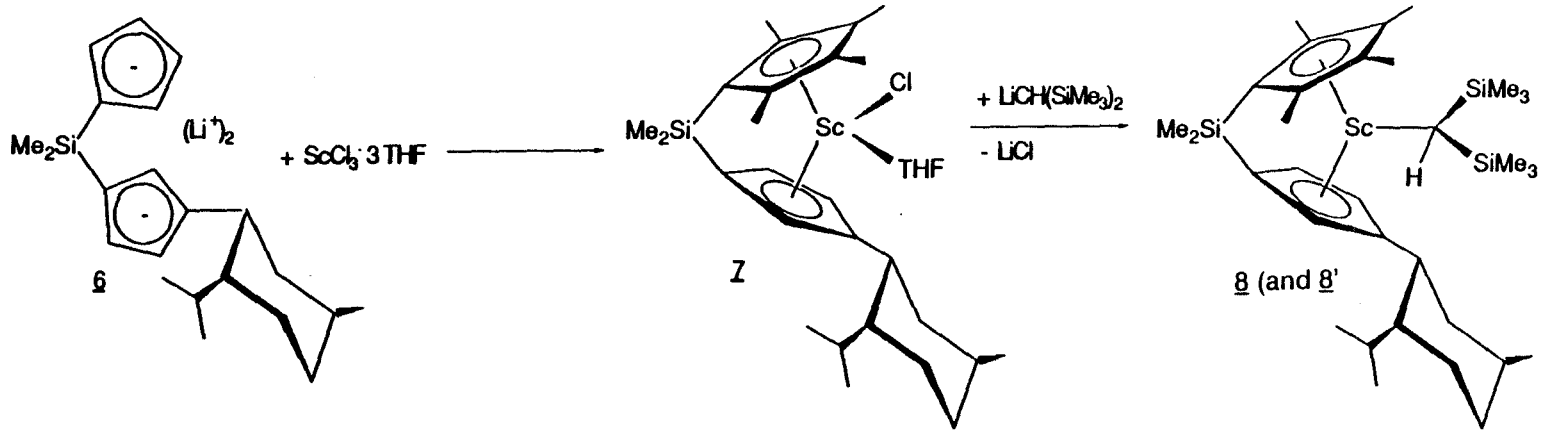
Results and Discussion

An "open-wedged" chiral scandocene complex was prepared by designing a ligand that utilizes a Me_2Si-bridge and incorporates an available resolved organic compound (1R,2R,5S)-menthyl, from the chiral "pool." The synthesis of this ligand is straightforward and is shown in Scheme 2.2. Reduction of 2,3,4,5-tetramethyl-2-cyclopentenone with $LiAlH_4$ yields 2,3,4,5-tetramethyl-2-cyclopentanol. Subsequent dehydration of the alcohol produces 1,2,3,4-tetramethylcyclopentadiene in moderate yield. The lithium salt, 1, is prepared by deprotonation with *n*-butyllithium and treated with dichlorodimethylsilane to give $Me_2Si(C_5Me_4H)Cl$, 2, which can be isolated as an oil. This starting material allows the synthesis of an asymmetric [Me_2SiCp_2] ligand. The second Cp ring to be added contains the chiral natural product, (1R,2R,5S)-menthyl. This ligand can be synthesized readily, as shown in Scheme 2.2. Commercially available (1S,2R,5S)-(+)-menthol is first converted to the (1S,2R,5S)-(+)-menthyl tosylate derivative with *p*-toluenesulfonyl chloride. It is subsequently treated firstly with LiCp to produce the (1R,2R,5S)-menthylcyclopentadienyl compound (Cp^m), 3, and secondly, treated with *n*-butyllithium to give the lithium salt, 4. 4 and 2 can be condensed to produce the mixed ring ligand, 5, which is deprotonated to give the dilithium salt, 6.

6 can be complexed to scandium according to Scheme 2.3 to give the scandocene complex, 7, that has a chloride as well as a solvent (THF) of coordination present. A more convenient starting material, 8, can be prepared from 7 by metathesis of the chloride with the bulky lithium reagent, $(Me_3Si)_2CHLi$ (see Scheme 2.3). The presence of the chiral menthyl group provides the opportunity for two diasteriomers (8 and 8') to form, which can be distinguished by the inequivalency in the ^1H NMR spectrum of the two trimethylsilyl (Sc-CH(SiMe_3)(SiMe_3')) groups. The integration of the four trimethylsilyl methyl resonances indicates that the diasteriomers are formed in roughly equal proportion with only a slight excess of one (8%).[4]

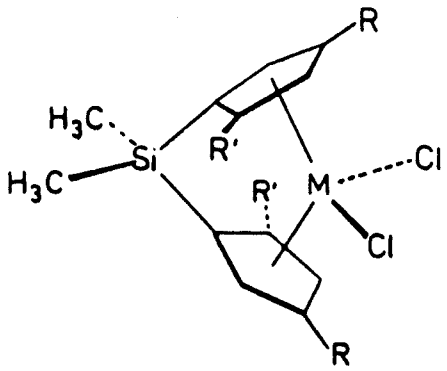


Scheme 2.2. Synthesis of 6.

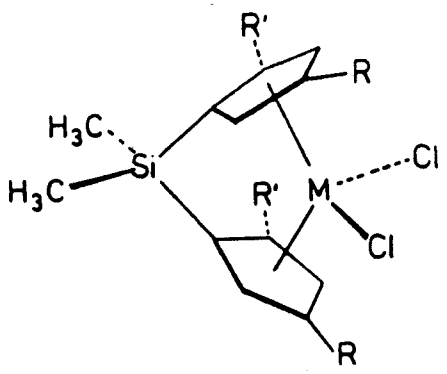


Scheme 2.3. Synthesis of 8 and 8'.

In related work, Brintzinger *et al.* have reported the formation of diasteriomeric zirconium complexes with dimethylsilylene-bridged, symmetrically disubstituted Cp rings, as shown in Figure 2.2.[5] They were able to separate the racemic and *meso* isomers by fractional recrystallization and carried out an investigation of the effect of alkyl Cp-substituents on the isomeric ratios.



rac

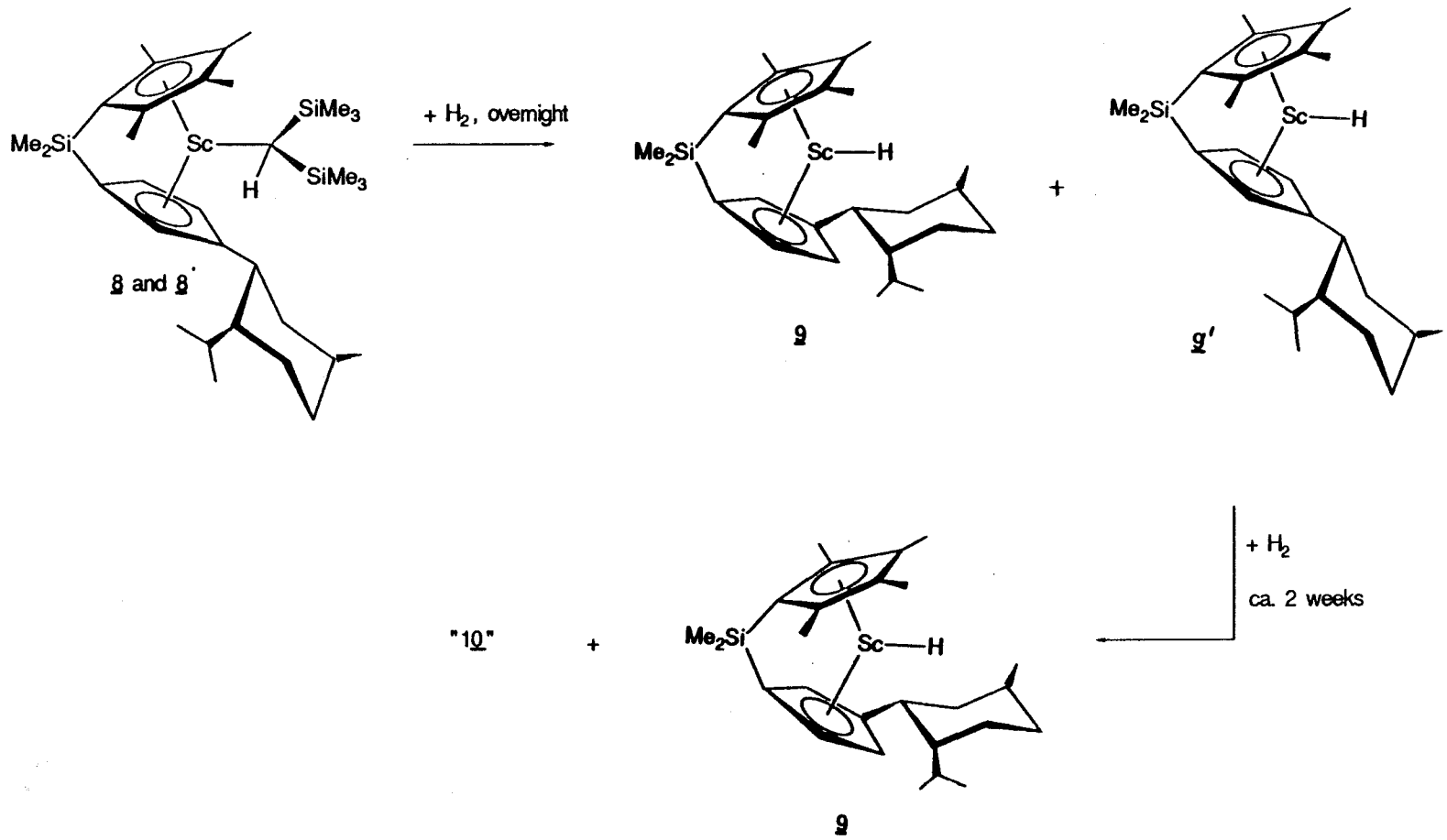


meso

R^1 =	$C(CH_3)_3$	$Si(CH_3)_3$	$C(CH_3)_2C_6H_5$	$C(CH_2)_5C_6H_5$	$C(CH_3)$
R^2 =	H	H	H	H	CH_3
rac/*meso*	1/1	1/1	1/1	1/1	2/1

Figure 2.2. Racemic and *meso* isomers of dimethylsilylene-bridged zirconocenes.

When 8 and 8' are stirred in benzene under 4 atmospheres of hydrogen overnight, a pair of diasteriomeric isomers of the scandium hydride complex are formed, 9 and 9' (see Scheme 2.4). These are easily distinguished by the inequivalency of the three downfield protons on the Cp^m ring. When allowed to stir for longer periods of time (up to two weeks), one of the hydride diasteriomers converts to the other, which will be (arbitrarily) assigned as 9. If rapid stirring does not occur, or if there is insufficient hydrogen present, a small amount of a third complex appears (see Scheme 2.4). The ^1H NMR spectra for the mixture of diasteriomers and the resolved diasteriomer are shown in Figure 2.3a and 2.3b, respectively.



Scheme 2.4. Synthesis of 9 and 9' and the conversion of 9' to 9.

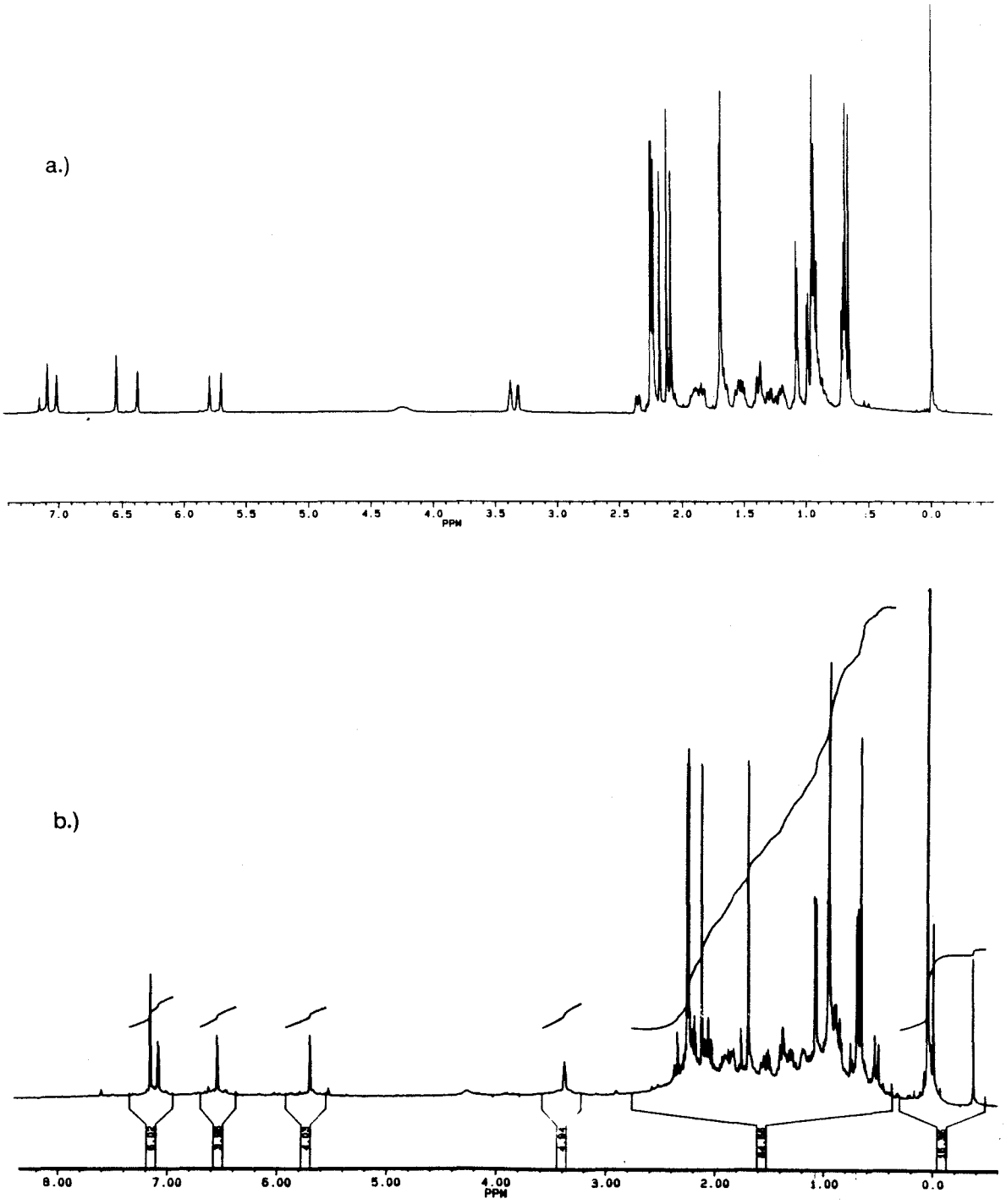


Figure 2.3a and 2.3b. ^{1}H NMR spectra of both isomers 9 and 9' (a), and only one isomer, 9' (b).

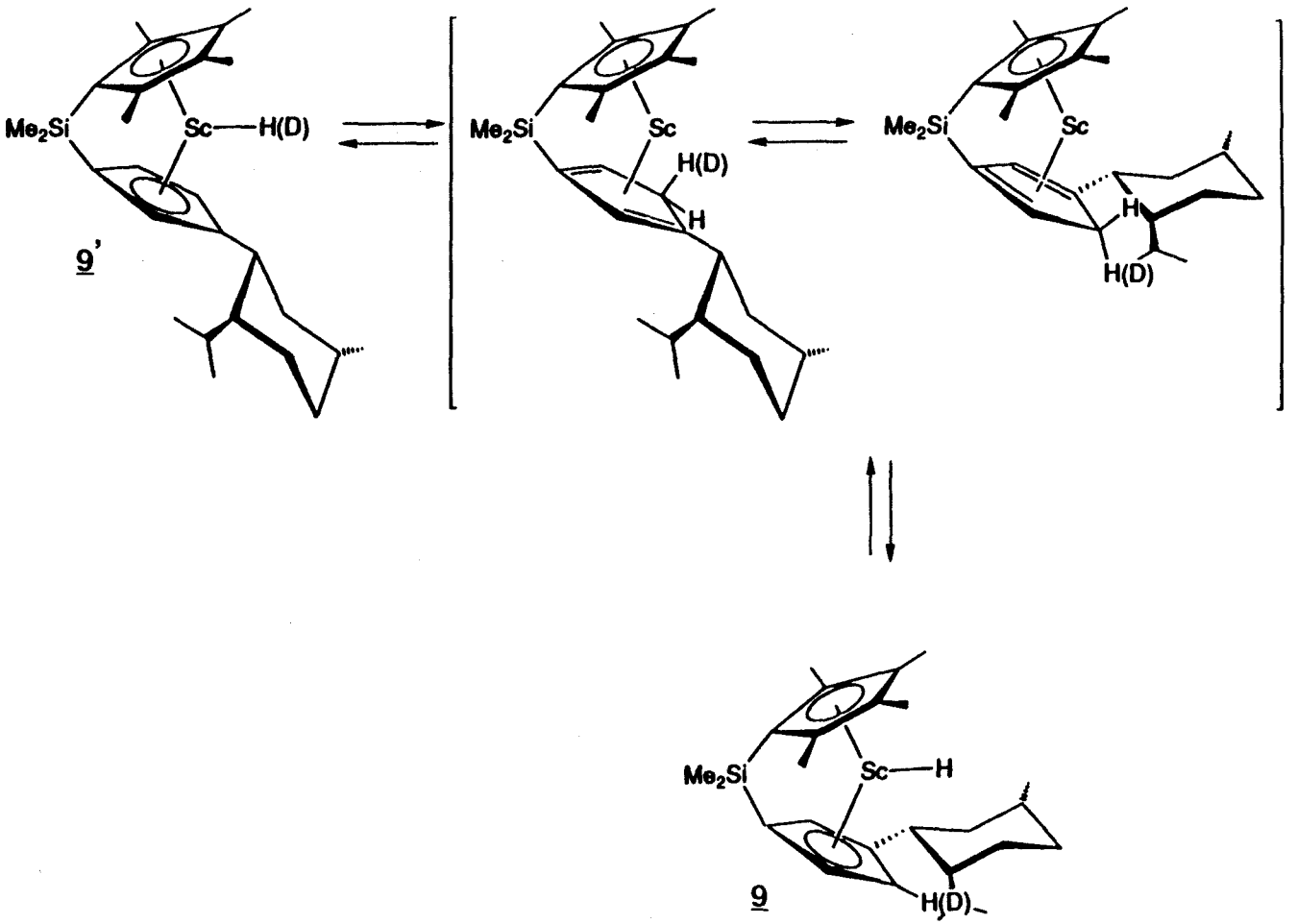
It is not known whether 9 and 9' are monomeric or dimeric; however, the related complex $[DpScH]_2$ is formulated as a dimeric species based on a molecular weight determination made by ebulliometry.[4] "$[OpScH]_x$" is not stable in the absence of a trimethylphosphine ligand.[4] Unfortunately, 9 is not stable in solution in the absence of hydrogen for the required time period to make a molecular weight determination. It is formulated here as a monomer because of the extremely bulky Cp^m ligand, but the possibility exists that it is in fact a dimeric species.

The hydrogen-promoted conversion to one scandium hydride diasteriomer is quite fortuitous and yields a resolved chiral complex without the necessity of fractional recrystallization, chromatography or other techniques for diasteriomeric separation.

In an effort to understand exactly how this resolution occurs, mechanistic studies were undertaken. It was initially proposed that the interconversion of 9'to 9 involved a simple H Sc-to-Cp migration. Were this the case, then if 9 and 9' were stirred under 4 atmospheres of deuterium, deuterium would be washed into the ring protons on the Cp^m ligand (see Scheme 2.5).

Accordingly, 9 and 9' were allowed to stir under a deuterium atmosphere for an extended period of time (up to 2.5 months) with periodic recharging of deuterium. The reaction was monitored by ^1H and ^2H NMR. The isomerization was considerably slowed, and the only incorporation of deuterium that was seen was into the isopropyl group of the menthyl moiety. This does not appear to have anything to do with the isomerization process and is probably a secondary reaction.

In addition to the deuterium labeling experiment, a small amount of acid was added to the reaction to determine whether acid catalysis played a role. The addition of even trace amounts of HCl produced an entirely different product and this was not pursued.

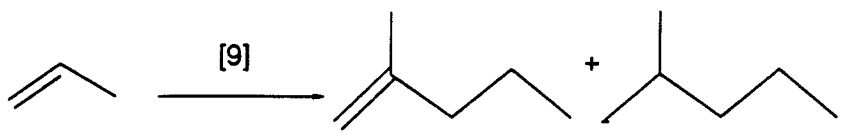


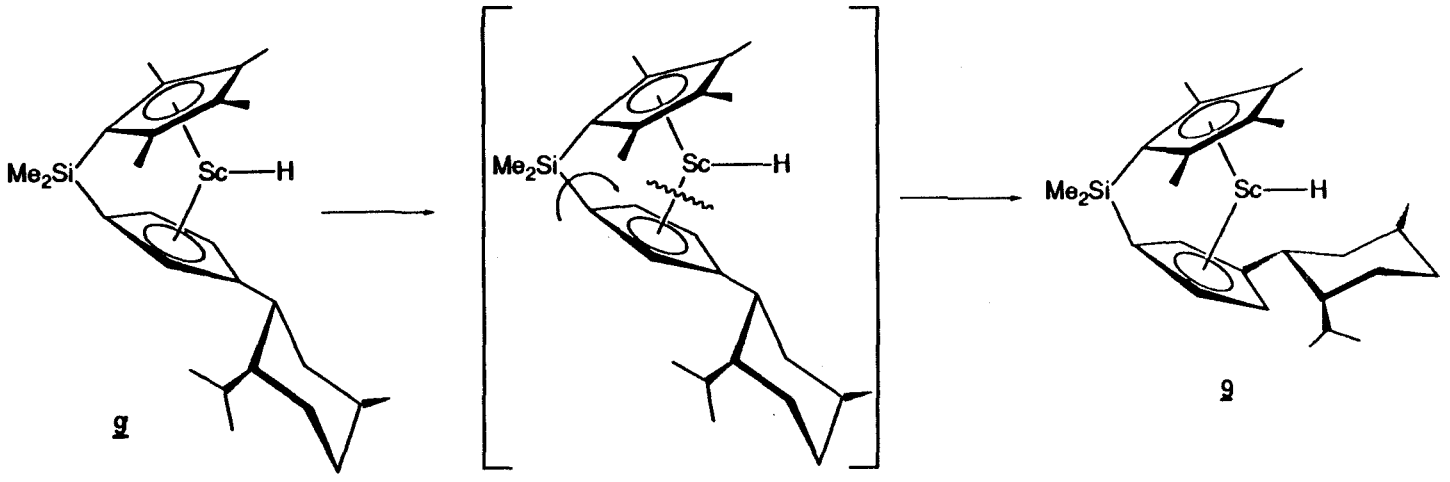
Scheme 2.5. The mechanism initially proposed for the isomerization of 9' to 9.

In an effort to determine whether light might play a role in assisting one of the Cp ligands to undergo homolysis and subsequent rotation and recoordination, three experiments were done under controlled conditions. A mixture of 9 and 9' were sealed in NMR tubes in benzene-d_6 under 4 atmospheres of hydrogen. One tube was exposed to lab light only. A second tube was kept in the dark, and the third tube was irradiated for 2.25 hours with a 1000 Watt lamp. The irradiated sample showed no isomerization, but did show considerable hydrogenation of the benzene-d_6 solvent. The samples that were kept in the dark and exposed to normal lab light began to isomerize in an identical fashion. Thus, it does not appear that a light-induced Sc-Cp^m homolytic cleavage mechanism is operative.

At this point, there is no positive evidence for an explanation of the mechanism of conversion from 9'to 9; what *is* known is that hydrogen is necessary for the conversion, the mechanism does not involve an H Sc-to-Cp migration, it is not acid-catalyzed and light does not promote the isomerization. A suggested mechanism for the isomerization is shown in Scheme 2.6. For the isomerization of 9' to 9 to occur, the Sc-Cp^m bond in 9' must be broken and the ligand allowed to rotate about the dimethylsilylene bridge-Cp^m bond. Recoordination of the opposite face of the Cp^m ligand affords the other diasteriomer, 9.

With the resolved chiral scandium hydride complex, 9, in hand, it was necessary to determine if 9 would promote the same kinds of olefin dimerization, cyclization and hydrogenations as $(DpScH)_2$ and OpScH(PMe_3). Accordingly, 9 was treated with 20 equivalents of propene in a sealed NMR tube, as shown in Equation 2.3.

(2.3) excess 

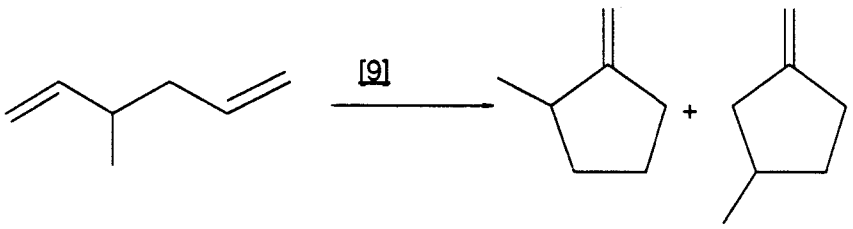


Scheme 2.6. A mechanism showing the steps that *must* occur for 9' to convert to 9.

By comparison with authentic samples, it was established that 9 will dimerize and hydrogenate propene to 2-methyl-1-pentene and 2-methylpentane. Apparently 2-methylpentane was formed as a consequence of the decomposition of 9. With the reactivity established, it was necessary to select a prochiral substrate to determine if it would be possible to achieve chiral control over these reactions.

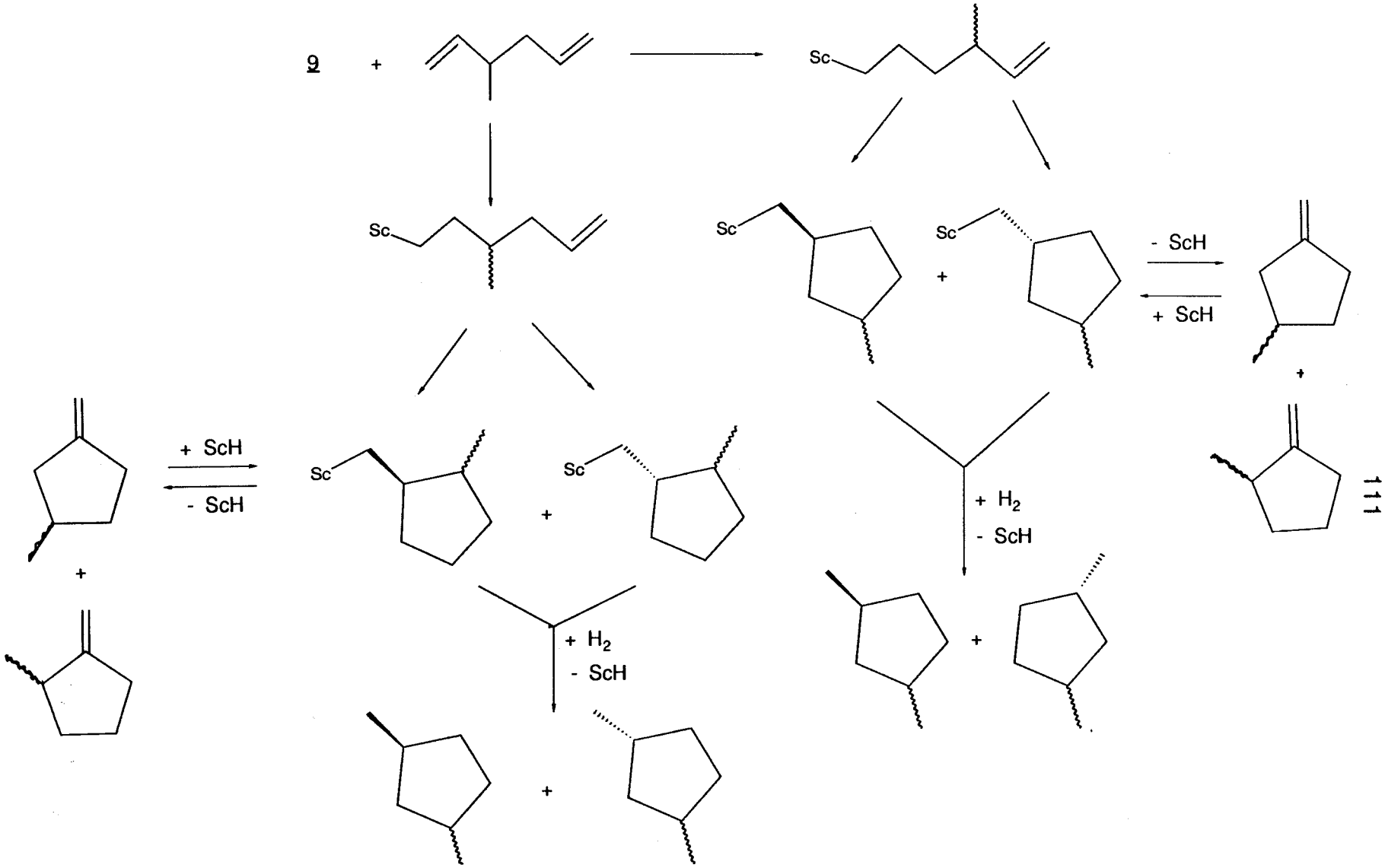
Initially, the prochiral diolefin 3-methyl-1,5-hexadiene was selected as the substrate of choice; 9 was treated with 20 equivalents of the substrate according to Equation 2.4.

(2.4)



Comparison of the ^{1}H and ^{13}C NMR spectra with authentic samples showed the products to be 2-methyl-*exo*-methylene cyclopentane and 3-methyl-*exo*-methylene cyclopentane, as expected. Unfortunately, the choice of 3-methyl-1,5-hexadiene as a test substrate presented many problems. The ring-closure step can occur from either face, creating one chiral site; however, the chiral center in the 3-methyl position may be too far removed from the reaction site to exert any great influence, and the subsequent decomplexation of the substrate produces an identical compound (see Scheme 2.7). On the other hand, hydrogenation after the cyclization step, which is also possible from either face, creates another opportunity for chiral control. Unfortunately, there are numerous possible chiral products (see Scheme 2.7).

A further problem with this system is that the only way to establish that any steric control over the products has occurred is by polarimetry. Although this method is commonly used to establish enantiomeric purity, it is not ideal. Enantiomeric purities are established by comparison with samples of known rotation, but small amounts of contamination can substantially change the rotations leading to spurious results.[5] Separating enantiomers by use

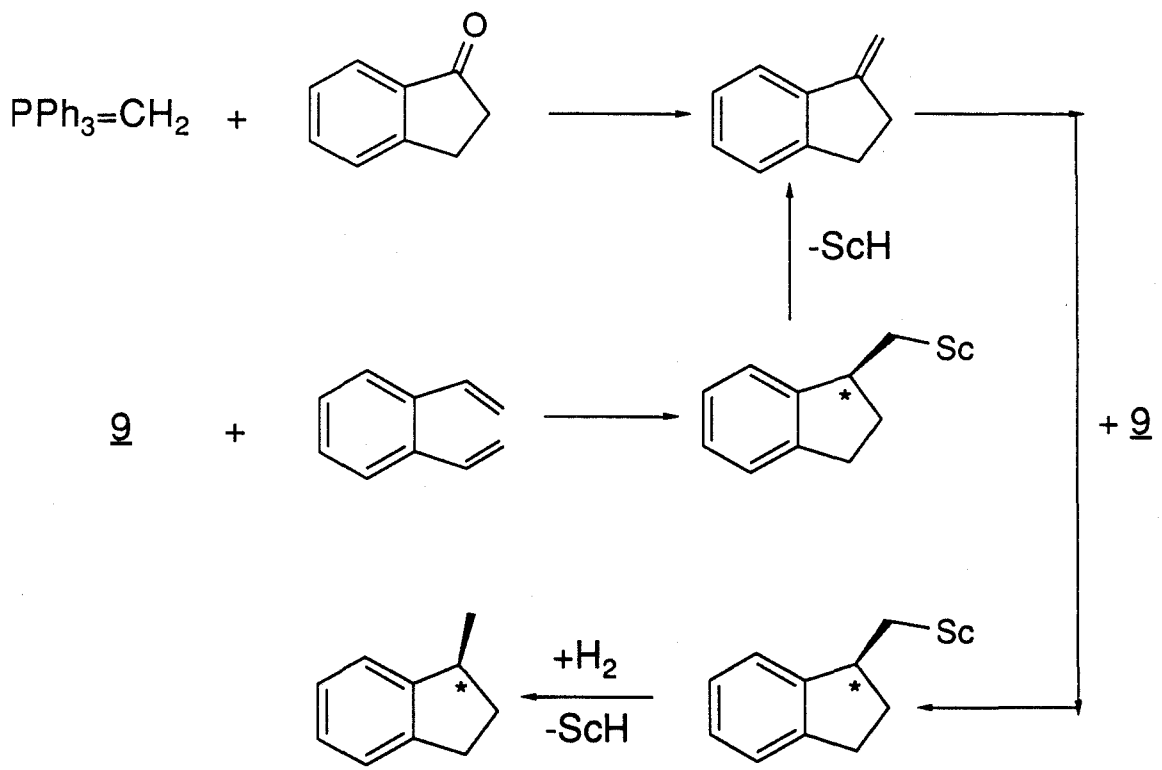


Scheme 2.7. The numerous possible chiral products from the hydrogenation of 3-methyl-1,5-hexadiene by 9.

of lanthanide shift reagents and establishing the enantiomeric purity by integration is considered much more reliable.[5] Furthermore, the only rotational standard available for this system is (+)-3-methyl-cyclopentanone. Because of these problems, another substrate was sought.

Divinylbenzene was selected as the next substrate to examine. Cyclization of divinylbenzene would create a chiral site with direct participation by the metal center (see Scheme 2.8). Unfortunately, divinylbenzene is not available commercially in a pure state, and all attempts to further purify it failed. Attempts were also made to synthesize divinylbenzene from the corresponding diketone and the appropriate Wittig reagent. It was not possible to obtain sufficiently pure divinylbenzene by this method either. Fortunately, however, it was not necessary to start with divinylbenzene. As shown in Scheme 2.8, the product of the cyclization of divinylbenzene is methylene indane, and it is the hydrogenation of *this* that is the stereodifferentiating step of the reaction. The intermediate complex 11 is identical whether or not the starting material used is divinyl benzene or methylene indane, so it is quite possible to start the asymmetric reaction with methylene indane rather than with divinyl benzene. Accordingly, methylene indane was synthesized from the corresponding ketone by treatment with Wittig reagent (see Scheme 2.8). Numerous attempts were made to produce very pure methylene indane. Success was achieved by never allowing the reaction to rise above room temperature. The purity of the methylene indane was assayed by GC and IR.

The reaction of 9 with methylene indane under 4 atmospheres of hydrogen proceeded smoothly to yield methyl indane. A maximum of four turnovers was achieved. In order to determine that the hydrogenation was accompanied by steric control, it was necessary to employ a silver/ chiral lanthanide combination of NMR shift reagents to distinguish the enantiomers. Methylindane is an ideal candidate for this kind of analysis because it has an aryl group that can bond strongly to a silver shift reagent (which will in turn bond to a chiral lanthanide shift reagent), and the methyl group on the indane ring is unique.



Scheme 2.8. The asymmetric hydrogenation of methylene indane by 9.

In 1981 and 1984, Mannschreck and Offermann reported the silver/lanthanide-induced ^1H NMR splittings of enantiomeric signals for various alkene and arene hydrocarbons.[6,7] (6,6,7,7,8,8,8-Heptafluoro-2,2,-dimethyl-3,5-octane-dionato)silver(I) (Ag(fod)), 12 (see Figure 2.4) was demonstrated to form complexes with arenes and alkenes, which are in an equilibrium in solution that is fast on the NMR time scale.[8] The silver complexation shifts and spreads proton resonances to lower field. Chiral recognition is achieved by the addition of a chiral lanthanide shift reagent such as (+)-tris(3-heptafluorobutyryl-D-camphorato)ytterbium(III) ($Yb(hfbc)_3$), 13 (see Figure 2.4). $Yb(hfbc)_3$ bonds to the silver complex of the alkene or arene and imparts chiral recognition despite the "dilution" of the optically active environment around the substrate.[6]

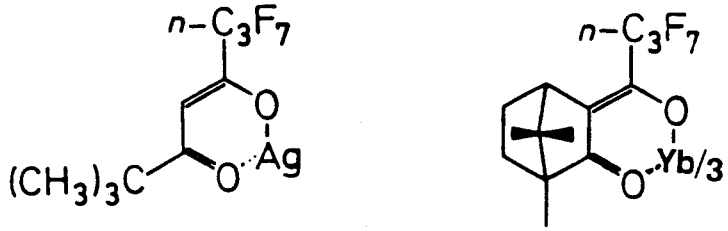


Figure 2.4. ^1H NMR shift reagents, 12 and 13.

The initial studies to determine feasibility of distinguishing the enantiomers of methylindane by ^1H NMR were done with the commercially available racemate of methylindane. After much experimentation with different lanthanide reagents and combinations of reagents and concentrations, optimal splitting of the enantiomeric methyl groups was achieved by using a $CDCl_3$ solution that was 0.1 M in methyl indane, 0.05 M in 12 and 0.2 M in 13. The ^1H 500 MHz spectra of pure methylindane and the mixture are shown in Figure 2.5a and 2.5b, respectively.

In order to determine the enantiomeric purity of the methylindane produced from the reaction of 9 with methylene indane, it was first necessary to separate the organic product from the organometallic complex. The first attempt was made by distilling the volatiles away from the

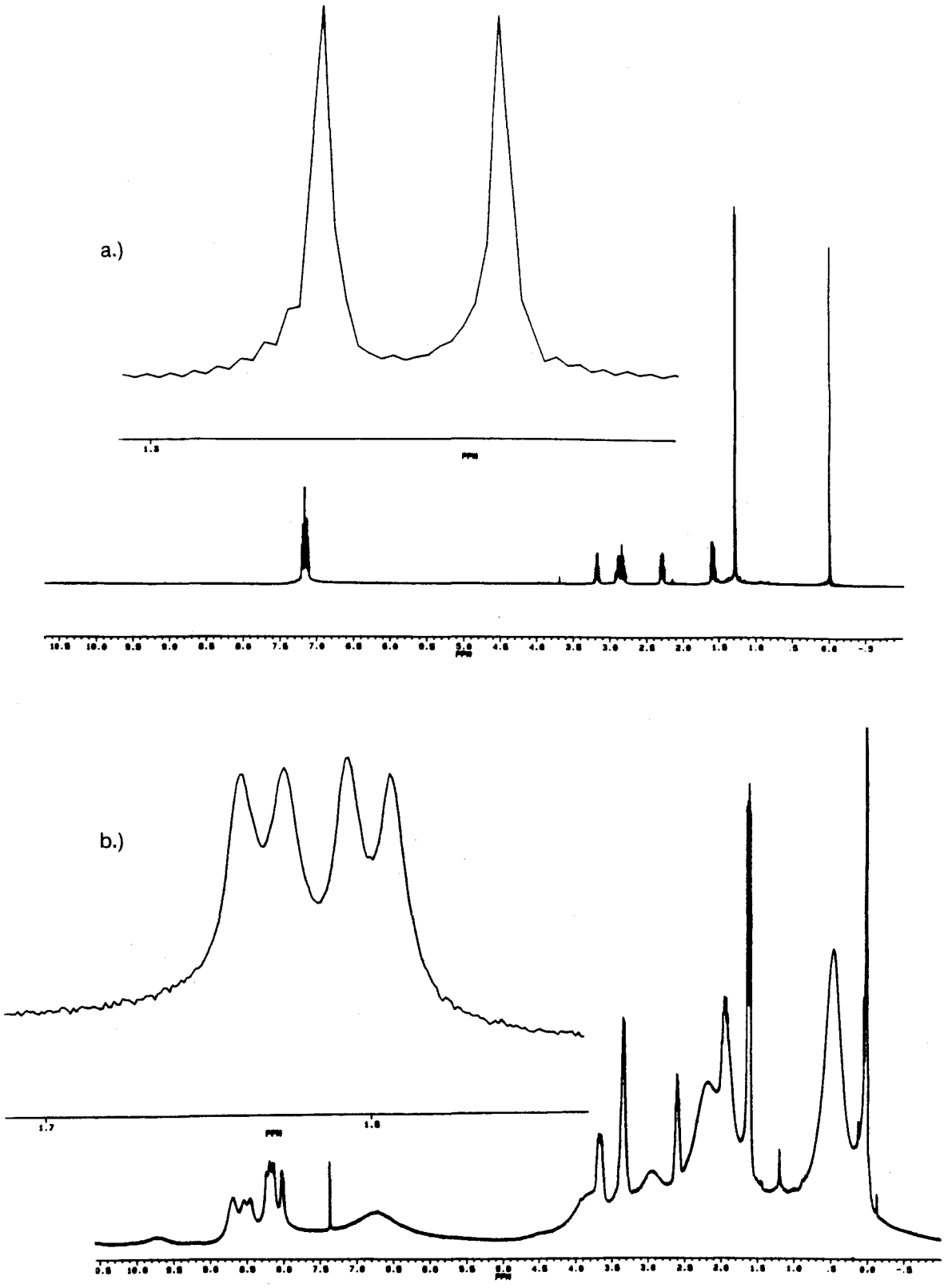


Figure 2.5a and 2.5b. The ^{1}H NMR spectrum of methylindane (a), and methylindane in solution with 12 and 13 (b).

reaction mixture; this failed because of the decomposition of the ligand into volatile organic fragments that were carried over by the distillation. It was necessary to quench the reaction mixture with air, reduce the solvent amount at 0°C, and run the solution through a silica gel plug or on silica gel plates by elution with a 70/20 mixture of hexanes and diethylether. Methylindane has an R_f value of .9 with this solvent system and can be easily recovered from silica gel.

The recovered methylindane was dissolved as a 0.1 M solution in $CDCl_3$ with 0.05 M 12 and 0.1 M 13. (In this case the optimal separation was given by these ratios *versus* the methylindane standard, which was optimized at 0.2 M 13, *vide supra*). The ^1H NMR of the methyl region is shown in Figure 2.6. The best enantiomeric selectivity achieved was 67-33%, which is an e.e. of 34%, which is comparable to the best e.e.'s reported by other systems for asymmetric hydrogenations of simple olefins(see Chapter 1).

Commercial methylindane was dissolved as a 0.1 M solution in $CDCL_3$ with 0.05 M Ag(fod) and 0.1 M $Yb(hfbc)_3$, and ^1H NMR spectra were obtained under the above conditions. The enantiomeric methyl groups of the methylindane integrated as 49-51%. In another control experiment, $(DpScH)_2$ was also reacted with methylene indane under hydrogen pressure, subjected to the same work-up procedures and dissolved as a 0.1 M solution in $CDCl_3$ with 0.05 12 and 0.1 M 13. The methyl peaks of the enantiomers integrated as 50.2-49.8%. These experiments clearly indicate that 9 does impart steric control to the hydrogenation of a prochiral olefin.

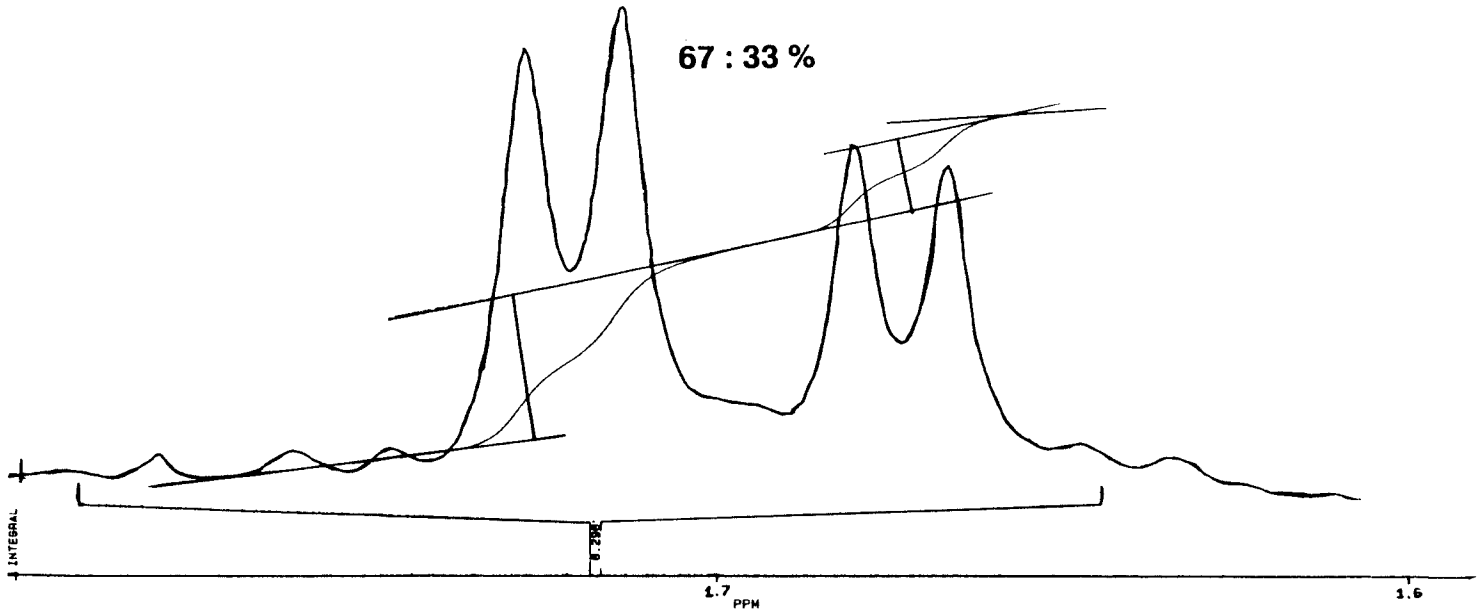


Figure 2.6. An e.e. of 34% for the hydrogenation of methylene indane by 9, as shown by ^{1} NMR.

Conclusions

It has been demonstrated that a resolved chiral scandium hydride complex, 9, can be synthesized from readily available starting materials, utilizing a chiral ligand available from the natural product "pool." It has been shown that this complex will induce the asymmetric hydrogenation of a prochiral olefinic substrate. An enantiomeric excess of 34% was determined by a powerful ^{1}H NMR technique utilizing a silver/lanthanide co-reagent system to separate enantiomeric signals. Although an enantiomeric excess of 34% is comparable to the best of other values reported for the asymmetric hydrogenation of a simple olefin, it is not high enough to be of use commercially. These kinds of processes become commercially feasible only as the enantiomeric excess approaches 90-100%. It may, however, be possible to increase the selectivity of the catalyst, 9, by optimizing conditions. In some cases, both temperature increases and decreases have been reported to result in greater sterioselectivity.[10]

Experimental

Materials

All manipulations were carried out by using either high vacuum or glove-box techniques.[11] Hydrogen, argon and deuterium were purified before use by passing through a MnO over vermiculite and activated 4A sieves column. Propene (Matheson) was degassed by several freeze-pump-thaw cycles prior to use. Benzene, toluene, petroleum ether, 3-methyl-1,5-hexadiene (Aldrich), and perdeuterobenzene were vacuum-transferred from $LiAlH_4$ or 4A sieves prior to use. Diethyl ether, tetrahydrofuran and perdeuterotetrahydrofuran were stored over benzophenone ketyl and vacuum-transferred before use. PPh_3CH_3Br was recrystallized from isopropanol before use. Methanol, *n*-butyllithium, scandium oxide, indanone, dimethyldichlorosilane, Yb(hfbc)$_3$, Ag(fod) and (1S,2R,5S)-(+)-menthol were used as received. The methylindane (Dixon) that was used as an NMR standard was used as received. $LiCH(SiMe_3)_2$[12], $ScCl_3 \cdot 3THF$[13], $[DpScH]_2$[4] and (1R,2R,5S)-menthylC_5H_4[14] were all prepared according to literature procedures.

Physical Measurements

^1H NMR spectra were recorded on Varian EM 390 (90 MHz) and Brucker WM500 (500.13 MHz) spectrometers. Elemental analyses were performed by the analytical facility at the California Institute of Technology. Gas chromatogragh analyses were carried out using a Perin-Elmer 8410 instrument and a RSL-150 (Alltech) column.

Syntheses

$Me_2Si(C_5Me_4)Cl$, 2. C_5Me_4HLi (10.0 g, 78.1 mmol) was suspended in tetrahydrofuran (150 ml) and cooled to -78°C. Me_2SiCl_2 (9.7 ml, 80 mmol), was added *via* syringe against an argon counterflow. The mixture was warmed to room temperature and stirred for two hours. The

solvent was removed *in vacuo* and replaced with petroleum ether (100 ml). Lithium chloride was removed by filtration, and the petroleum ether was removed *in vacuo,* leaving the product as a colorless liquid that solidified upon cooling to -40°C. Yield: 16 g. (95%). ^{1}H data: see Table 2.1.

$Me_2Si(C_5Me_4)$((1R,2R,5S)-menthyl$C_5H_3)Li_2$, 6. (1R,2R,5S)-MenthylC_5H_3Li (2.93 g, 13.9 mmol), dissolved in tetrahydrofuran (40 ml) was added to $C_5Me_4SiMe_2Cl$ ((3.0 g, 14 mmol) dissolved in tetrahydrofuran (20 ml). The solution was stirred for twelve hours, and the solvent was removed *in vacuo* and replaced with petroleum ether (50 ml). The lithium chloride was removed from the solution by filtration and the petroleum ether was removed *in vacuo*, leaving an oily liquid. Diethylether was added (80 ml), the solution was cooled to -78°C, and *n*-butyllithium (1.6 M solution in hexanes, 30 ml, 48 mmol) was added. The solution was warmed slowly to room temperature and allowed to stir for a further three hours. The solvent was removed *in vacuo* and replaced with petroleum ether (100 ml). The product was collected as a white solid, washed with fresh petroleum ether and dried *in vacuo*. Yield 5 g (98%). ^{1}H NMR data: see Table 2.1

$Me_2Si(C_5Me_4)$((1R,2R,5S)-menthylC_5H_3)ScCl•THF, 7. 6 (10.24 g, .026 mmol) and $ScCl_3$•3THF (9.57 g, .026 mmol) were dissolved in toluene (150 ml). The mixture was refluxed overnight; the solvent was removed *in vacuo* and replaced with petroleum ether. The solution was filtered to remove lithium chloride and the solvent was removed, leaving a white powdery residue, which was dried *in vacuo*. Yield: 13.8 g, (60%). ^{1}H NMR data: see Table 2.1.

$Me_2Si(C_5Me_5)$((1R,2R,5S)-menthylC_5H_3)ScCH$(SiMe_3)_2$, 8. (1.0 g, 20 mmol) and $(Me_3Si)_2CHLi$•0.5Et_2O (0.4 g, 20 mmol) were stirred for four hours in toluene (30 ml). The solvent was removed *in vacuo* and replaced with petroleum ether (50 ml). Lithium chloride was removed from the solution by filtration, and the solvent was removed *in vacuo* and replaced with diethylether. Cooling to -78°C afforded yellow crystals of the product. Yield: .30 g (70%).

Anal. calcd. for $C_{33}H_{59}Si_3Sc$: C, 67.75; H, 10.16. Found: C, 67.79; H, 9.66. ^1H NMR data: see Table 2.1.

$Me_2Si(C_5Me_4)((1R,2R,5S)$-menthyl$C_5H_3)ScH$, 9, 9'. 8 (0.5 g, .85mmol) was dissolved in benzene (25 ml) and the solution was loaded in a thick-walled glass bomb. One atmosphere of hydrogen was admitted to the evacuated vessel at -196°C (ca. 4 atmospheres at room temperature), and the system was allowed to warm slowly to room temperature. The solution was agitated rapidly overnight (for isolation of both diasteriomers) or for as long as two weeks (for isolation of only one diasteriomer). The reaction was monitored by ^1H NMR. The solvent was removed at 0°C (to prevent decomposition), leaving a yellow solid, which was dried *in vacuo* and quickly transferred to the freezer in the glove-box for storage. Yield: .35 g (87%). Anal. calcd. for $C_{26}H_{42}SiSc$: C, 76.07 ; H, 9.90. Found: C, 71.52; H, 9.17. ^1H NMR data: see Table 2.1.

Dimerization of Propene. 9 (0.04 g, .076 mmol) was dissolved in .5 ml benzene in a sealable NMR tube. 269.7 Torr (20 eq.) was subjected to three freeze-pump-thaw cycles and then admitted to the evacuated NMR tube. The NMR tube was subsequently flame-sealed. The solution was stirred overnight, cracked open and the volatile products vacuum distilled away from the organometallic product. ^1H NMR data: see Table 2.1.

Cyclization and hydrogenation of 3-methyl-1,5-hexadiene. The procedure for the dimerization of propene was followed using .04 g (.076 mmol) 9 and .205 ml (10 eq.) of 3-methyl-1,5-hexadiene. The same procedure was followed for the hydrogenation experiment with the exception that one atmosphere of hydrogen was admitted to the NMR tube at -196°C. ^1H NMR data: see Table 2.1.

$PPh_3{=}CH_2$. 34 g (.112 mol) of PPh_3CH_3Br were loaded in the glove-box with 3.0 g (.125 mol) oF NaH into a flask. 250 ml of THF were cannulated onto the solids at -78°C. The resultant slurry

was allowed to warm slowly to room temperature a further 3.5 hours. The solution was filtered, the solvent removed and the solid product was dried *in vacuo*. Yield: 25.8 g (84%).

Methylene indane. To 4.79 g (.017 mol) of $PPh_3{=}CH_2$ in a THF solution, a THF solution of 2.29 g (.017 mol) indanone was added at -78°C. The solution was allowed to warm to room temperature and stirred for three days. The THF was removed at 0°C *in vacuo* and the resultant solids were extracted multiple times with petroleum ether. The petroleum ether was removed at 0°C, leaving the product as a viscous oil. ^{1}H NMR data: see Table 2.1.

Hydrogenation of methylene indane by $(DpScH)_2$. .05 g (.144 mmol) of $(DpScH)_2$ was dissolved in 2 ml of benzene in a thick-walled glass vessel. .025 ml (5 eq.) of methylene indane was added. One atmosphere of hydrogen at -196°C was admitted to the evacuated vessel. The solution was agitated briskly overnight. Most of the solvent was removed *in vacuo,* the vessel was opened and the remaining solution was loaded onto silica gel thin layer chromatography (TLC) plates and eluted with a 70:20 solution of hexanes/diethylether. The organic products were collected as a band with an $R_f$value of ca. 0.9.

Hydrogenation of methylene indane by 9. The procedure described above was followed, using 0.02 g of 9 and 0.016 g (4 eq.) of methylene indane.

Preparation of NMR samples with shift reagents. A solution of $CDCl_3$ that was 0.1 M in substrate, 0.05 M in 12 and 0.1 M in 13 was centrifuged to settle particulate matter. Clear solution was taken from the top of the centrifuge tube and used for the ^{1}H NMR studies.

Table 2.1. ^{1}H NMR Data.

Compound	Assignment	δ (ppm)
$Me_2Si(C_5Me_4)Cl$, 2	$C_5(C\underline{H}_3)_4Si(CH_3)_2Cl$	1.7(s) ; 1.9(s)
(90 MHz, C_6D_6)	$C_5(CH_3)_4Si(C\underline{H}_3)_2Cl$	0.12(s)
$Me_2Si(C_5Me_4)((1R,2R,5S)$-menthyl$C_5H_3)Li_2$, 6		
(500 MHz, THF-d_8)	$(C\underline{H}_3)_2Si$	0.39(s)
	$C_5(C\underline{H}_3)_4$	2.1(s) ; 1.9(s)
	$C_5\underline{H}_3$	5.85(m) ; 5.77(m) ; 5.73(m)
$Me_2Si(C_5Me_4)((1R,2R,5S)$-menthyl$C_5H_3)ScCl\cdot THF$		
(500 MHz, THF-d_8	$(C\underline{H}_3)_2Si$	0.71(s) ; 0.68(s)
		0.66(s) ; 0.64
	$C_5(C\underline{H}_3)_4$	1.90(s) ; 1.88(s) ; 1.85(s)
		1.83(s) ; 1.81(s) ; 1.78(s)
		(2 signals under THF-d_8)
	$C_5\underline{H}_3$	6.27(t) ; 6.08(t) ; 5.58(t)
		5.51(m) ; 5.38(t)
$Me_2Si(C_5Me_4)((1R,2R,5S,)$-menthyl$C_5H_3)ScCH(SiMe_3)_2$, 8		
(500 MHz, C_6D_6)	$C_5\underline{H}_3$	7.22(m) ; 7.16(m) ; 6.13(m)
		5.87(m) ; 5.63(m) ; 5.34(m)
	$C_5(C\underline{H}_3)_4$	2.02(s) ; 2.01 ; 1.98(s)
		1.87(s) ; 1.81(s) ; 1.78(s)

		1.72 ; 1.67
	$SiCH(C\underline{H}_3)_2$	0.32(s) ; 0.27(s)
		0.08(s) ; 0.04(s)
	$Si(C\underline{H}_3)_2$	0.55(s) ; 0.82(s)

$Me_2Si(C_5Me_4)$((1R,2R,5S)-menthylC_5H_3)ScH, 9, 9'

(500 MHz, C_6D_6)	$C_5\underline{H}_3$	7.08(t) ; 7.01'(t) ; 6.54(t)
		6.37'(t) ; 5.80'(t) ; 5.70(t)
	$C_5(C\underline{H}_3)_4$	2.25(s) ; 2.24(s) ; 2.23'(s)
		2.17'(s) ; 2.12(s) ; 2.08'(s)
		1.69'(s) ; 1.68(s)
	$Si(C\underline{H}_3)_2$	0.95(s) ; 0.93'(s)
		0.68'(s) ; 0.60(s)
	$Sc\underline{H}$	3.36(b) ; 3.31'(b)

Methylindane Standard	$C_6C_3(C\underline{H})_3$	(1.28, 1.29)(d)
(500 MHz, $CDCl_3$)		

0.1 M methylindane + 0.05 M 12 + 0.1 M 13

(500 MHz, $CDCl_3$)	$C_6C(C\underline{H}_3)$	(1.71, 1.73)(d)
		(1.67, 1.68)(d)

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