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Dihapto binding of aromatic molecules by π-basic transition metal complexes: development of alternatives to the $\{Os(NH_3)_5\}^{2+}$ fragment

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Abstract

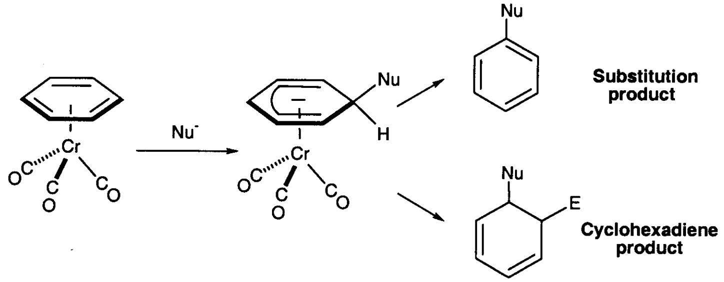
Dihapto-coordination of aromatic ligands by electron-rich transition metals can effectively dearomatize the bound aromatic molecule. The pentaammineosmium(II) system forms thermally stable η^2-complexes with a variety of arenes and aromatic heterocycles, and has been used for a variety of organic transformations on the bound aromatic fragments. The systematic variation of isoelectronic rhenium(I) systems has provided the necessary electronic and steric characteristics needed for a less expensive, chiral alternative to the $\{Os(NH_3)_5\}^{2+}$ system. The $\{TpRe(CO)(PMe_3)\}$ system has been shown to form stable dihapto complexes with furan, thiophene and naphthalene. Accordingly, the $\{TpRe(CO)(PMe_3)\}$ fragment and analogous {TpRe(CO)(L)} fragments represent the first class of asymmetric surrogates to the pentaammineosmium(II) system.

Keywords: Osmium; Rhenium; Dearomatization; Aromatic; Electrophilic

1. Introduction

Aromatic molecules represent a potentially useful pool of synthons for a variety of organic syntheses. The availability of a number of aromatic compounds with a diversity of functionalization patterns, both internal and external to the ring system, coupled with the often inexpensive cost of these reagents render them highly attractive as precursors. In addition, the unsaturated ring systems offer the opportunity to further derivatize the cyclic carbon skeletons. Given the prevalence of alicyclic systems in a wide range of naturally occurring compounds and other carbogenic compounds of interest, the selective dearomatization of aromatic molecules is an important synthetic goal. The Birch reduction is an example of a useful dearomatization methodology, and extensive effort has been invested in the development of this procedure for general applications [1,2].

Within the realm of organometallic chemistry, a variety of coordination modes exist for the binding of aromatic molecules to transition metals. Hexahapto complexes of aromatic compounds with the $\{Cr(CO)_3\}$ fragment activate the aromatic ligand toward nucleophilic addition [3–5], and other metal carbonyl systems have shown similar reactivity [6–8]. In addition to activation toward nucleophilic attack, the electron-withdrawing nature of the metal carbonyl system serves to stabilize the anionic intermediate. Thus, depending on the particular conditions, the production of either substituted aromatic compounds or dearomatized cyclohexadienes can be achieved (Scheme 1).

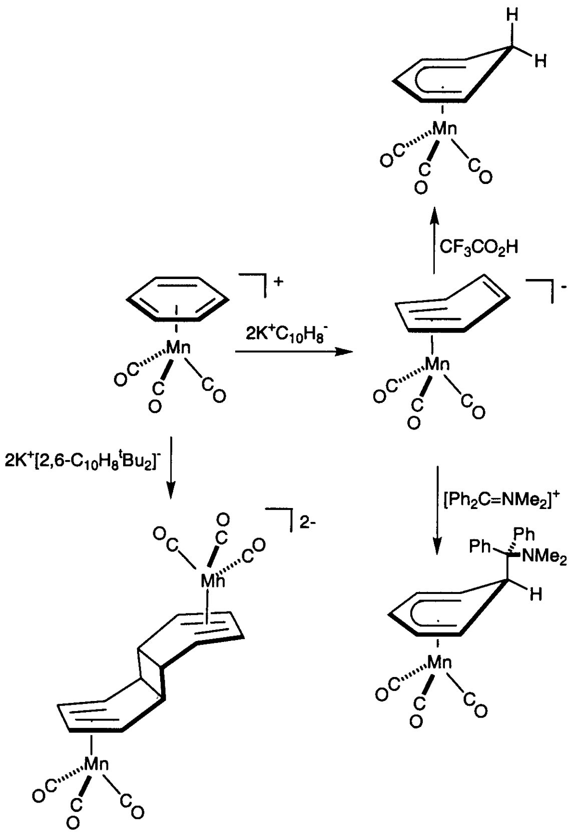


Scheme 1.

Apart from the hexahapto coordination mode so often found for metal carbonyl systems, η^4-coordination of several aromatic ligands (e.g. benzene, naphthalene and anthracene) has been observed for the $\{Mn(CO)_3\}^-$fragment [9–13]. Accordingly, two-electron reduction of the parent hexahapto system $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ yields the monoanion $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$(Scheme 2). The η^4-benzene system is activated toward electrophilic addition of iminium salts, protonation and $[2+2]$ cyclodimerizations.

For electron-rich transition metal complexes, an alternative coordination mode for aromatic compounds has been observed. A small number (cf. the prevalence of η^6-aromatic complexes) of dihapto-bound aromatic complexes has been reported (vide infra). Complementary to η^6-aromatic complexes, η^2-coordination of aromatic compounds can activate the bound moiety toward electrophilic addition. Dihapto-binding of aromatics results in a synergistic bonding interaction between the aromatic ligand and the metal center. Thus, the aromatic moiety acts both as a Lewis base (donates electrons into the metal center from a filled π-orbital) and as a π-acid (receives electron donation from a metal dπ-orbital into an empty π^*-orbital) (Scheme 3). Metal dπ back-bonding into a π^*-orbital of the aromatic ligand disrupts the aromaticity of the ligand.

To our knowledge, the only transition metal system which has been demonstrated to be synthetically useful for organic transformations of η^2-bound aromatic ligands is the $\{Os(NH_3)_5\}^{2+}$ fragment [14]. Indeed, this metal fragment is the only known system which forms thermally robust η^2-complexes with arenes and aromatic heterocycles. The binding of an aromatic compound to the osmium metal center has been shown to activate the organic ligand toward the addition of electrophiles,



Scheme 2.

Lewis basic donation from filled π-orbital into empty and symmetrical metal orbital

Aromatic ligand acting as π-acid via empty π*-orbital interacting with filled dπ orbital of metal

Scheme 3.

and the arenium intermediate is stabilized by coordination to the electron-rich metal. As a result, subsequent nucleophilic addition and dearomatized products can be produced. Significantly, the osmium system can also direct the regio- and stereoselectivity of the addition reactions.

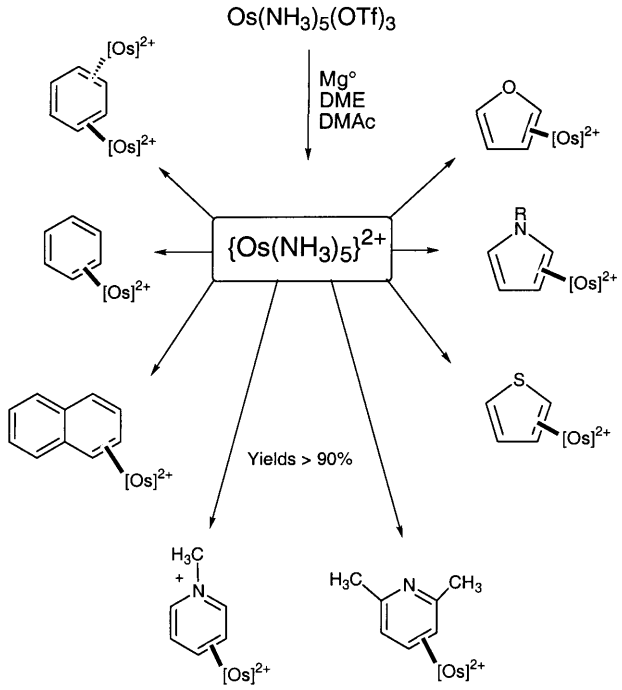
Since the organic transformations utilizing the $\{Os(NH_3)_5\}^{2+}$ fragment have previously been reviewed [14], the emphasis of this manuscript will be the development of surrogate metal systems which exhibit similar binding and activation abilities to those of the $\{Os(NH_3)_5\}^{2+}$ fragment. For the purposes of continuity, the current review will briefly cover the binding ability, characteristics, and reactivity of pentaammineosmium(II). In addition, the limitations of the $\{Os(NH_3)_5\}^{2+}$ system, examples of previously reported η^2-aromatic complexes and their relation to our research goals, and our efforts toward the development of π-basic Re(I) complexes for the binding and activation of aromatic compounds will be discussed in detail.

2. Review of the $\{Os(NH_3)_5\}^{2+}$ fragment

2.1. *Scope of binding and discussion of the $\{Os(NH_3)_5\}^{2+}$ fragment*

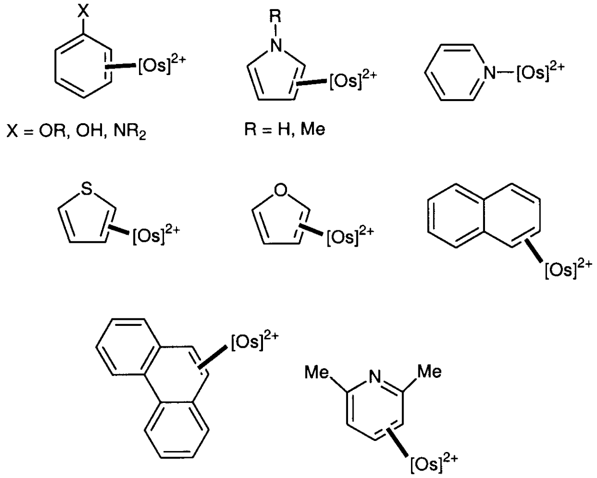
Access to the $\{Os(NH_3)_5\}^{2+}$ system is attained via reduction of the readily available Os(III) precursor $[Os(NH_3)_5(OTf)][OTf]_2$ (OTf = trifluoromethanesulfonate) [15]. Typically, the procedure utilizes magnesium as a reducing agent and *N*,*N*-dimethylacetamide (DMAc) as the solvent. The d^6 osmium(II) metal center shows a predilection for dihapto-coordination of a large purview of aromatic compounds. Examples of η^2-aromatic complexes include benzenes [16,17], polyarenes [18], anisoles [19,20], anilines [21–24], furans [25–27], thiophenes [25,28] and pyrroles, [25,29–34] (Scheme 4). In the case of pyridine, the aromatic ligand is bound only through the heteroatom [35]. However, 2,6-lutidene shows a proclivity toward η^2 binding through two carbons of the heterocycle [36]. Contrary to many η^2-aromatic species (vide infra), the osmium complexes are relatively substitution inert. For benzene, the rate of exchange shows little dependence on the incoming ligand, and this fact reflects a mechanism for aromatic substitution, which is primarily dissociative in nature.

Several factors contribute to the unique coordination chemistry demonstrated by the pentaammineosmium(II) system. The five ammine ligands are strong σ-donors and are incapable of significant π-interaction with the metal center. The combination of the electron-donating ligand set and the d^6 configuration renders the osmium center strongly reducing and a pertinacious π-base. As a result, the osmium metal shows a strong disposition to bind any ligand with π-acidic character in the sixth coordination site. Evidence of osmium's surfeit of electron density can be seen upon comparing the regioselectivity of coordination of aniline versus pyridine. Both of these aromatic compounds can bind as two-electron donors either η^1 through nitrogen or η^2 through the aromatic ring. For aniline, η^1-binding through the amine nitrogen results in a strong σ-donating and poor π-acid ligand. As a result, aniline binds both η^2 through two ring carbons and η^1 though the amine nitrogen ($K_{eq} \sim 1$ at room temperature (r.t.) in CH_3CN) (Scheme 5). Pyridine, on the other hand, can act as a moderate π-acid in its η^1-bound coordination mode. Since nitrogen-bound pyridine can serve as a π-acid without disrupting aromaticity, this is the thermodynamically preferred coordination mode. Thus, the bond enthalpy gained by the electron-rich osmium upon η^2-coordination of aromatics compensates for the loss of aromaticity resulting from the subsequent bond localization.



Scheme 4.

Oxidative addition is typically observed with electron-rich complexes possessing unsaturated coordination environments. The d^6 configuration and strongly σ-donating ammonia ligands of the $\{Os(NH_3)_5\}^{2+}$ system result in a metal center which

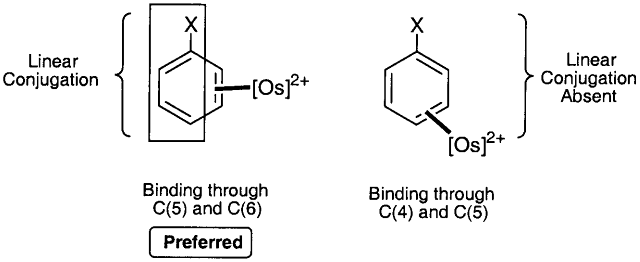


Scheme 5.

prefers an octahedral geometry [37]. Oxidative addition would require a seven-coordinate intermediate resulting in a significant reorganization and crowding of the ammine ligands.

2.2. Regiochemistry of coordination

Although sterics can play an important role in the ligand regioselectivity of aromatic binding, the electronic perturbation of the aromatic is generally the governing factor which dictates binding selectivity. For example, binding of six-membered arenes with a singly substituted ring (either electron deficient or electron withdrawing group) occurs at C(5) and C(6) to allow linear conjugation of the substituent with the unbound portion of the ring (Scheme 6). In contrast, pyridinium ions are bound preferentially across C(4) and C(5). Jones et al. have provided an insightful analysis of the regiochemistry of η^2-binding of aromatics [38]. Coordination is generally preferred at the site which disrupts aromaticity the least. For example, the binding of naphthalene is thermodynamically preferred at C(1) and C(2) over C(3) and C(4), and coordination of phenanthrene occurs preferentially across C(9) and C(10) (Scheme 5). As predicated by resonance structure arguments, five-membered heterocylces (thiophenes, furans or pyrroles) bind across C(4) and C(5) (Scheme 5).



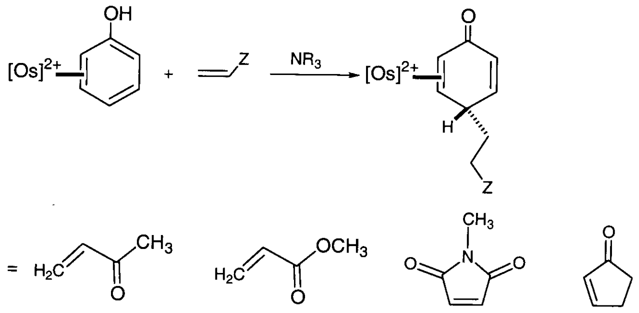
Scheme 6.

2.3. Reactions of $[Os(NH_3)_5(\eta^2\text{-aromatic})]^{2+}$ complexes

2.3.1. Arenes

Osmium complexes of phenols, anisoles and anilines are typically activated toward electrophilic addition at C(4). Addition at C(4) yields a product in which the uncoordinated portion of the π-system is in conjugation with the heteroatom (alcohol, methoxy or amine group). The 4H-arenium complexes are stabilized against rearomatization by the osmium metal center, and subsequent nucleophilic additions can be performed. A general feature of these addition reactions is that the reagent adds *anti* to the face of the aromatic ring bound to osmium.

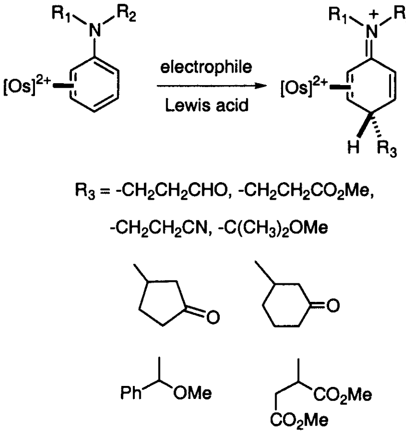
2.3.1.1. Phenols [39]. Phenol bound to $\{Os(NH_3)_5\}^{2+}$ undergoes base-catalyzed conjugate addition at C(4) with a variety of Michael acceptors (Scheme 7). The



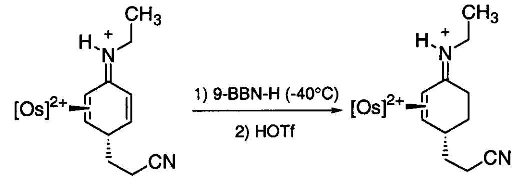
Scheme 7.

ability to deprotonate the bound phenol ligand renders it more reactive toward electrophiles than complexes of anisoles or anilines. The products from reaction with Michael acceptors are cyclohexadienones substituted at the 4-position. The 2,5-cyclohexadienone products fail to react with borohydride reagents or non-basic carbon nucleophiles. Starting with 4-substituted phenol complexes, electrophilic addition *ortho* to the hydroxy group is often thermodynamically preferred.

2.3.1.2. Anilines [24]. In contrast to phenol, deprotonation of the heteroatom of aniline is difficult. Thus, addition of electrophiles must be catalyzed by Lewis acids {BF_3, $Sn(OTf)_2$ or TBSOTf (TBS = *tert*-butyldimethylsilyl)} (Scheme 8). Examples of electrophiles which yield 4H-anilinium complexes include Michael acceptors, acetals and acylating reagents. Unfortunately, the 4H-anilinium complexes are stabilized to the point that they fail to react with non-basic carbon nucleophiles such as silyl ketene acetals and enol ethers. Furthermore, the use of basic nucleophiles yields rearomatizatized products via deprotonation (and formation of



Scheme 8.

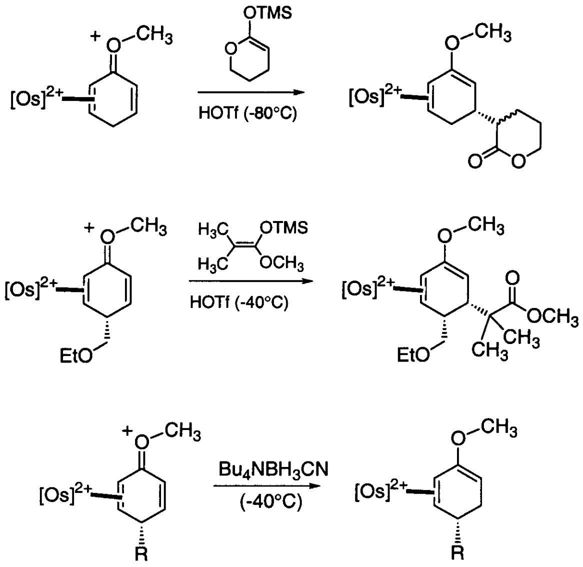


Scheme 9.

substitution product) or results in retroaddition of the electrophile. The 4H-anilinium complexes can be reduced to olefinic products upon reaction with Li(9-BBNH) (9-BBN = 9-borabicyclo[3.3.1]nonane) (Scheme 9).

2.3.1.3. Anisoles [40]. Reactions with anisole complexes of osmium must be performed at low temperature. The arenium products are highly reactive and a wealth of transformations can be accessed with this class of complexes to form substitution products, dearomatized systems, as well as annulated compounds. Alkylation of $[Os(NH_3)_5(\eta^2\text{-anisole})]^{2+}$ with a variety of electrophiles and subsequent deprotonation yields 4-substituted anisole complexes. Substitution reactions have been performed with a variety of β-unsaturated carbonyl compounds, Michael acceptors, acetals, orthoesters and nitrilium salts.

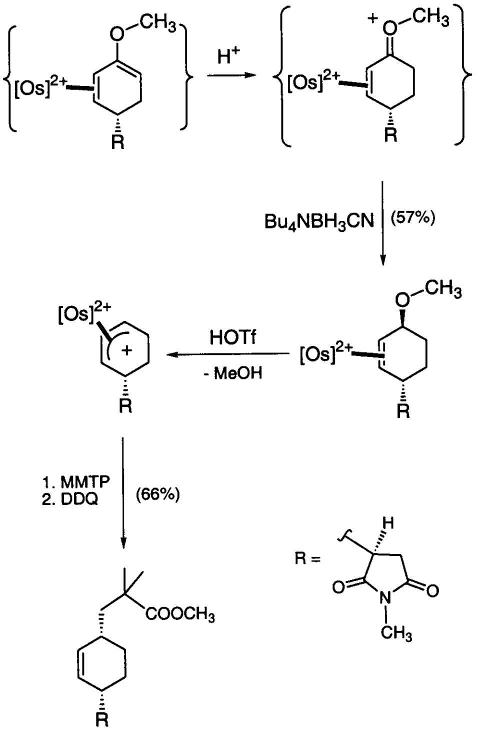
As mentioned previously, the 4H-anisolium complexes are extremely reactive and undergo C–C bond forming reactions with mild carbon nucleophiles. Stepwise treatment of anisole complexes of osmium with electrophile/nucleophile affords cyclohexadiene products (Scheme 10). The reduction of 4H-anisolium complexes



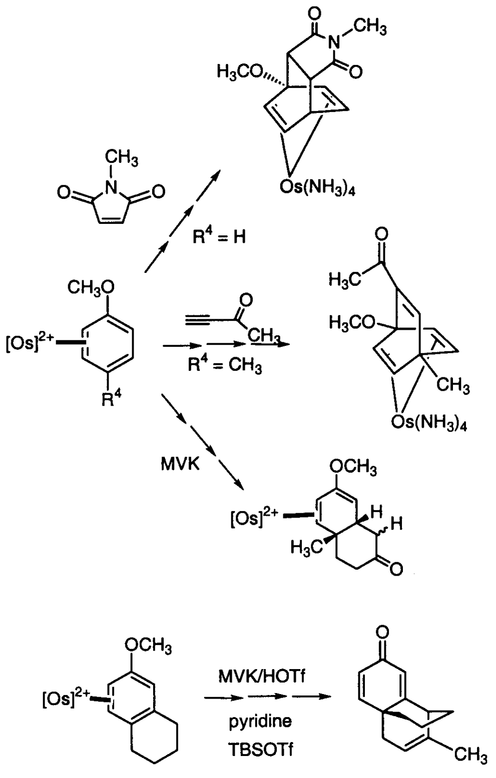
Scheme 10.

with a hydride source yields the corresponding cyclohexadiene. However, in the presence of acid the diene is further reduced to an allyl ether resulting in the elimination of methanol. This sequence provides a potential route for the synthesis of 1,4-disubstituted cyclohexenes (Scheme 11).

A wide range of cyclization reactions can be accessed starting with osmium η^2-anisole complexes. For example, the parent anisole complex reacts with *N*-methylmaleimide to ultimately yield bicyclo[2.2.2]octadienes (Scheme 12). Reaction of the 4-methylanisole complex with 3-butyn-2-one provides a route to an η^4-barrelene complex (Scheme 12). In acidic methanol, treatment of the 4-methylanisole complex with MVK (methylvinylketone) results in a net [4 + 2] Michael–Michael ring closure to yield a *cis*-decalin ring system (Scheme 12), and ensuing oxidation yields the organic decalin. Tricyclic systems can be obtained by reaction of the 6-methoxy-1,2,3,4-tetrahydronaphthalene complex with MVK/HOTf, pyridine and TBSOTf (Scheme 12). Finally, the 5,6-η^2-ring-bound methoxystyrene complex can be used for cycloaddition reactions. The unbound portion of the methoxystyrene resembles a vinylogous methoxydiene and reacts with dienophiles with high regio- and stereoselectivity. It should be noted that direct complexation of styrene compounds yields olefin bound species, and the methoxystyrene must be synthesized by an indirect route.



Scheme 11.

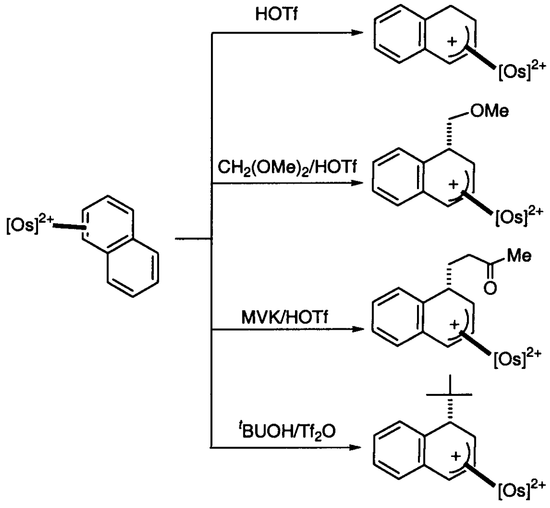


Scheme 12.

2.3.1.4. Naphthalenes [41]. The naphthalene complex of pentaammineosmium(II) has been utilized to synthesize 1,4-dihydronaphthalene compounds. Addition of electrophiles to [Os(NH_3)$_5$(η^2-naphthalene)] yields η^3-allyl complexes (Scheme 13). Examples of electrophiles, which are useful for this transformation include acids, acetals, alcohols (with triflic anhydride) and Michael acceptors. The resulting allyl cations are susceptible to nucleophilic attack to form 1,4-substitution products (Scheme 14).

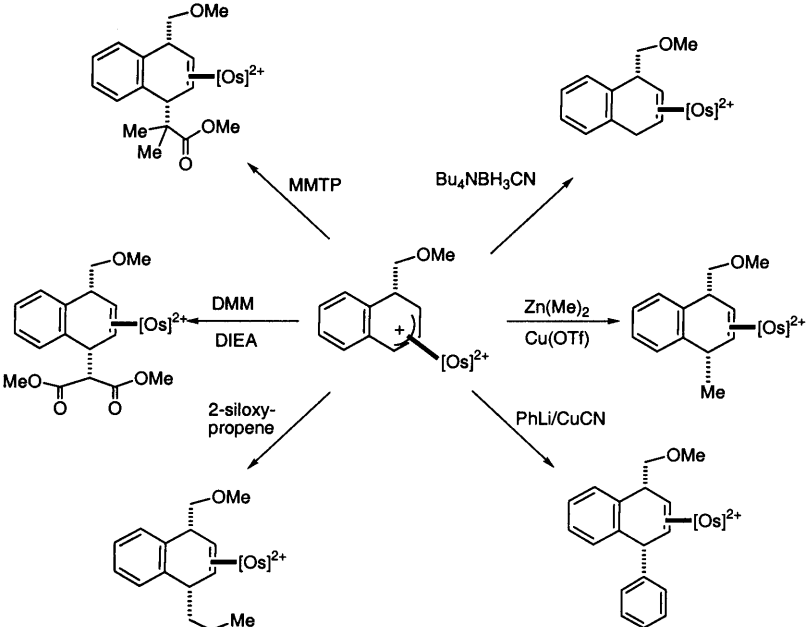
2.3.2. Heterocycles

2.3.2.1. Pyrroles [42]. There are three potential sites for electrophilic addition to osmium η^2-pyrrole complexes {nitrogen, C(2) and C(3)}. Pyrrole complexes of pentaammineosmium(II) have been observed to undergo electrophilic addition at either C(3) or nitrogen. Reaction at C(3) is generally thermodynamically observed, although nitrogen addition is sometimes found under kinetic conditions (typically with 'hard' electrophiles). Electrophilic addition at the β carbon has been achieved with nitrilium salts, acetic anhydride, aldehydes, ketones, acetals, Michael acceptors and alkyl triflates. Deprotonation of the 3H-pyrrolium complexes is often facile,

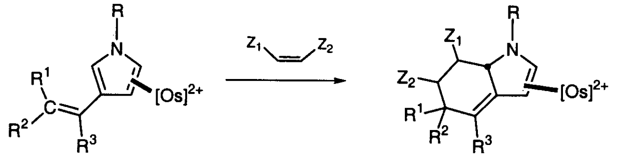


Scheme 13.

and a variety of 3-substituted complexes have been prepared. Alternatively, pyrrolines can be synthesized by nucleophilic addition to C(3) of the 3H-pyrrolium complexes (with cyanide or hydride as the nucleophile). This transformation cannot

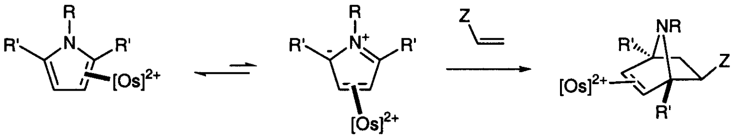


Scheme 14.



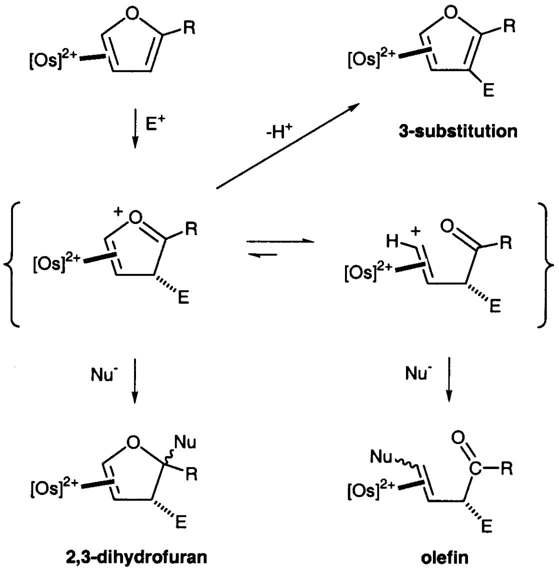
Scheme 15.

be accomplished with strongly basic nucleophiles (e.g. enolates), vinyl ethers, siloxyalkenes, or malonate anion. The synthesis of β-vinyl pyrroles and subsequent reaction with dienophiles provides a route to a variety of indole compounds (Scheme 15). In addition, the osmium pyrrole complexes are reactive with dipolarophiles. Even though coordination at C(4) and C(5) is thermodynamically favored, coordination of the 3,4-η^2 isomer is kinetically accessible. Thus, treatment of osmium pyrrole complexes with dipolarophiles yields 7-azabicyclo[2.2.1]heptene complexes (Scheme 16).



Scheme 16.

2.3.2.2. Furans [26]. Much like the pyrrole complexes, electrophilic addition to furan complexes of $\{Os(NH_3)_5\}^{2+}$ can occur at C(3) or the heteroatom, and addition at C(3) is generally thermodynamically preferred. However, the chemical reactivity of the osmium furan complexes is substantially more diverse due to the proclivity of the furan moiety to undergo ring-opening reactions. Thus, the 3H-furanium complexes which result from electrophilic addition can ring-open to form η^2-vinyl cations. The net synthetic result is that the furan complexes can be utilized to form 3-substitution products, 2,3-dihydrofurans or olefinic products (Scheme 17). For electrophilic additions with an electron-withdrawing group, the formation of substitution products is most likely due to the resulting acidity of the 3H proton of the furanium product. Interestingly, when methanol is used as the nucleophile for the formation of 2,3-disubstituted dihydrofurans, the methoxy substituent is oriented *syn* to the osmium fragment. This stereochemistry is in contrast to the majority of additions with the osmium system and reflects the reversibility of methoxide addition under acidic conditions (i.e. the thermodynamic product is the species with the methoxy group *syn* to the osmium and trans to the C(3) substituent). Reactions with nucleophiles are kinetically controlled and produce products in which the nucleophilic fragment is oriented *anti* to the osmium fragment. It is also possible to form bicyclic products via Michael–Michael aldol ring closures, as well as osmium carbyne complexes via ring opening processes (Scheme 18).

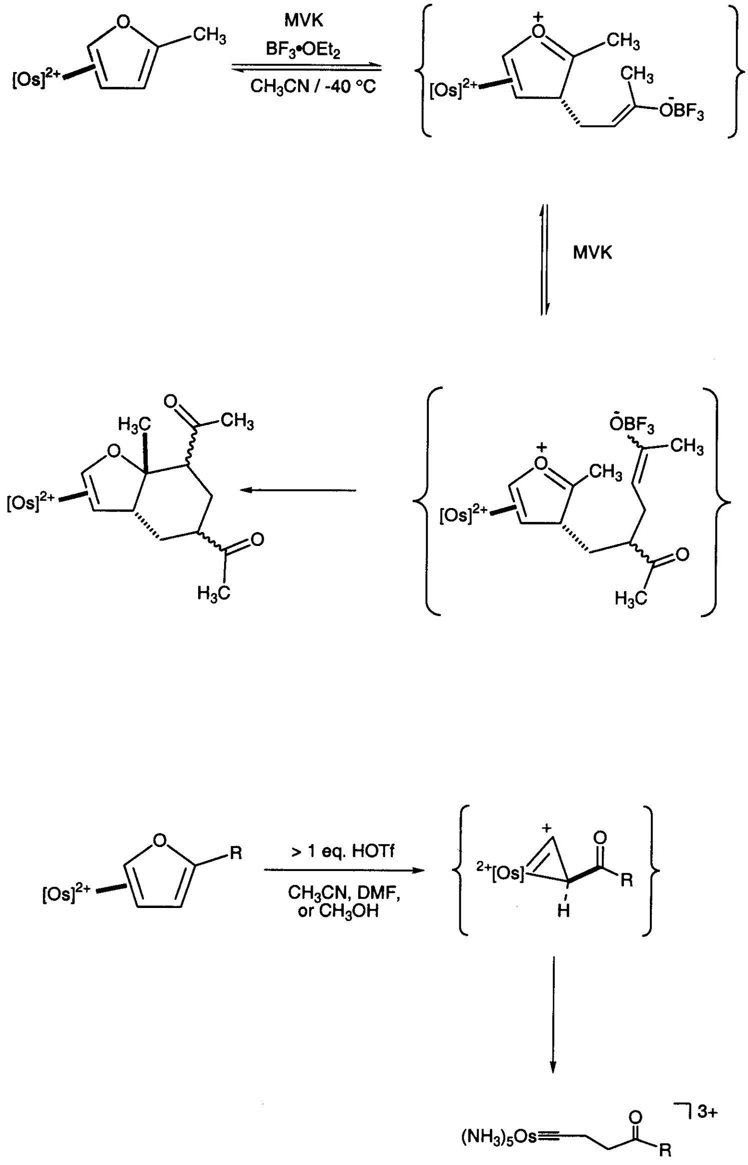


Scheme 17.

2.3.2.3. Thiophenes [43]. Similar to furan and pyrrole complexes, thiophene complexes of $\{Os(NH_3)_5\}^{2+}$ can add electrophiles at the ring or the heteroatom. However, in contrast to the other heterocycles, thiophene complexes undergo electrophilic attack primarily at C(2) rather than C(3). Addition of methyl cation to the sulfur atom of bound thiophene yields an η^2 thiophenium complex which is in equilibrium with its ring-opened vinyl cation isomer. The vinyl cation readily adds nucleophiles at C(5) to yield thiodiene compounds. In addition to electrophilic reactions, the ability to hydrogenate and desulfurize thiophene complexes of osmium has been demonstrated.

2.4. Limitations of pentaammineosmium(II) and desirable characteristics of a surrogate dearomatization agent

While the pentaammineosmium(II) system is an extremely versatile and potent π-base, it has several limitations which make finding a surrogate desirable. Perhaps one of the most easily recognized problems with applying the osmium system to organic synthesis is cost. While the cost of pentaammineosmium(II) is not exorbitant ($7/mmol) [44] in relation to many other heavy metal reagents, the fact that the system is used stoichiometrically makes finding a less expensive metal system imperative. Another problem with the pentaammine system is that several of the precursors and reagents (e.g. hydrazine) used to produce the $\{Os(NH_3)_5\}^{2+}$ precursor are known to be toxic or dangerous to handle. Most problematic in this regard is the OsO_4 starting material which is a relatively volatile solid [45]. Ultimately, the pentaammine system itself is less insidious than the precursors used to make it and



Scheme 18.

can be handled with relative ease. Nevertheless, the use of any heavy metal dearomatization agent in organic synthesis is of concern environmentally. Accordingly, judicious choice of alternate metals and ligands to ameliorate toxicity is important.

Chemically, the ancillary ammine ligands of $\{Os(NH_3)_5\}^{2+}$ present limitations. The most serious of these is the fact that it contains an achiral metal center. While recent advances in our laboratory have addressed this problem in a limited respect [40,46,47], the achiral environment of the pentaammine system restricts the ability of the osmium to promote enantioselective transformations on coordinated organic moieties. Furthermore, attempts to replace one of the ammonia ligands of the $\{Os(NH_3)_5\}^{2+}$ fragment with a chiral amine have led to a loss of aromatic binding ability by the metal as well as β-hydride elimination of the amine to form an η^2-iminium species [48,49]. The ammonia ligands are sterically quite favorable for coordination of aromatics, but their acidic nature hampers the range of nucleophiles and strong bases which can be used in subsequent additions to any coordinated organic ligand. Finally, the dicationic nature of the $\{Os(NH_3)_5\}^{2+}$ fragment reduces the solubility of osmium complexes in many common organic solvents, and hinders the use of several purification techniques (e.g. column chromatography with silica gel or alumina) as well as the range of organic reagents which can be employed in addition reactions.

The strengths and weaknesses found in the osmium system can be used as a guide for the next generation of dearomatization agents. The most important characteristics of the $\{Os(NH_3)_5\}^{2+}$ fragment which must be maintained in any surrogate include the use of a low-valent d^6 metal, the enforcement of an octahedral environment around the metal and the utilization of ancillary ligands which are primarily σ-donors. All of these factors influence the electronic environment at the metal by enhancing its electron-rich nature and ability to back-bond. In addition, an octahedral metal center is well-suited for subsequent additions to coordinated organic ligands since the metal itself is less susceptible to attack by an incoming electrophile or nucleophile. An octahedral coordination sphere also deters oxidative addition of any potential aromatic ligand. The use of σ-donor ligands (such as amines, pyridines, or phosphines) is desirable because they enhance the electron-rich nature of the metal and are also not particularly susceptible to attack by electrophiles. In comparison, cyclopentadienyl ligands are known to undergo electrophilic additions. With these criteria and the aforementioned limitations of the osmium system in mind, we turned our attention to the development of a rhenium(I) analog of the $\{Os(NH_3)_5\}^{2+}$ fragment.

3. Development of alternative dearomatization agents

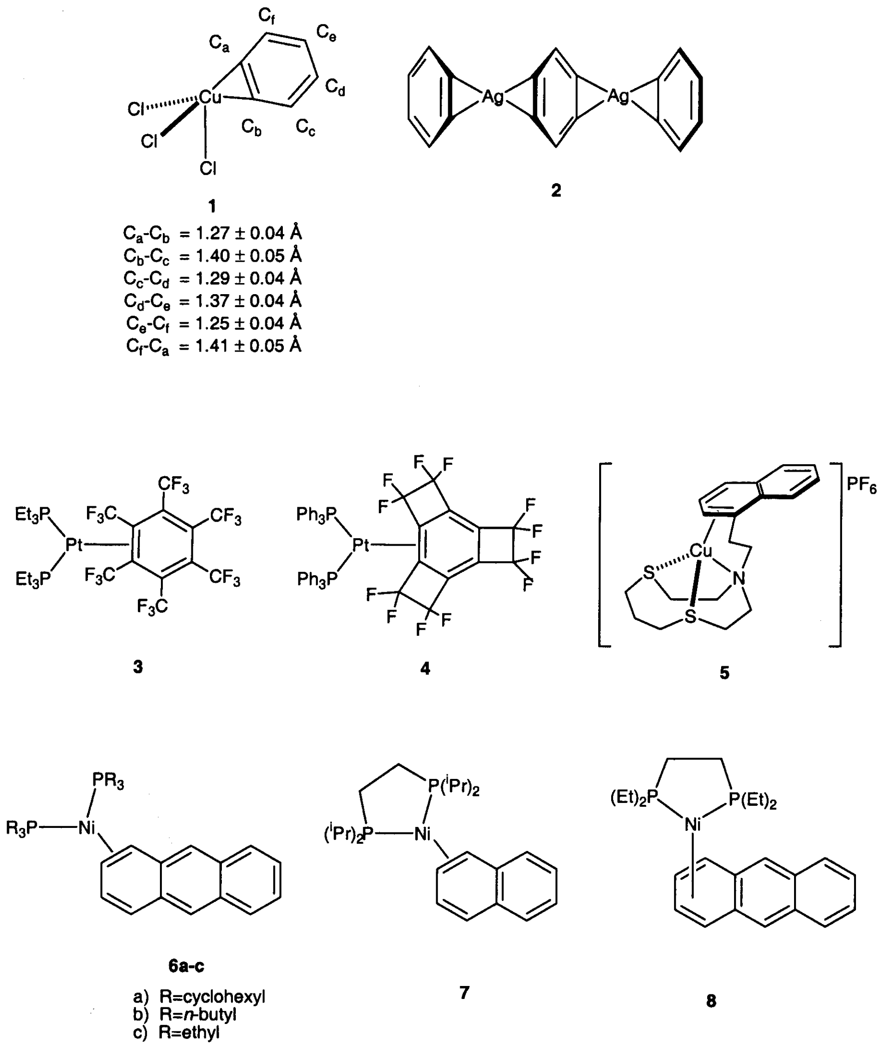
3.1. *Examples of η^2-coordination of aromatic molecules by transition metals*

Unlike the scattered examples of other transition metal fragments which bind aromatic ligands in a dihapto fashion, the pentaammineosmium(II) fragment forms thermally robust η^2-coordinated complexes with arenes and aromatic heterocycles (vide supra). The explanation for this lack of thermally stable dihapto-coordinated aromatic complexes arises primarily from the strict electronic characteristics required for the η^2-coordination mode. Simply, the metal center must be electron-rich enough to be a suitable π-base in order to stabilize the bond between the arene or aromatic heterocycle and the metal; however, the metal cannot be so electron-rich that it yields a stable C–H activated product of the aromatic molecule. Indeed, η^2-coordinated aromatic compounds have been postulated as intermediates in C–H activation sequences for some time [50]. Another more subtle requirement for dihapto coordination of aromatics by octahedral complexes involves a small steric profile for ligands *cis* to the coordination site of the aromatic ligand. This fact has become increasingly apparent from recent results in our laboratory in which small changes in the steric characteristics of ancillary ligands cis to the potential coordination site alter the ability of the metal to coordinate aromatic ligands (vide infra). Despite these restrictions, there are examples of η^2-coordinated aromatic complexes with a variety of metals including Cu(I), Ag(I), Ni(0), Pt(0), Ta(III), Nb(III), Rh(I), Ru(0), Ru(II), Os(II) and Re(I).

3.1.1. d^{10} *Systems of copper(I), silver(I), platinum(0) and nickel(0)*

The d^{10} systems of Cu(I) and Ag(I) represent some of the earliest characterized examples of η^2-coordinated arenes (Scheme 19). The crystal structure of $(C_6H_6)Cu(AlCl_4)$ (**1**) has been found to have alternating bond lengths for the benzene ring suggestive of a cyclohexatriene system although the deviations from those of free benzene are small [51,52]. This system is comprised of sheets of the monomer linked through copper-chloride bonds. The copper atom lies above the edge of one of the carbon–carbon bonds of the benzene ring and is not equidistant from the two carbon atoms. Silver perchlorate systems have been known to exhibit coordinating properties with arenes for some time. The simplest of these, $(C_6H_6)Ag(ClO_4)$ (**2**), was reported in 1950 and essentially involves alternating sheets of silver atoms with bridging benzene and perchlorate moieties [53]. Most of the Cu(I) and Ag(I) d^{10} systems are best described as ‘layered structures’ [51] and are of interest to the development of dearomatization reagents only from an historical perspective due to their relatively weak disruption of aromaticity and chemical lability. Perhaps more relevant to the current discussion is the recent example of a copper(I) naphthalene complex. The copper atom of the $[CuL][PF_6]$ system {L = *N*-(2-(1-naphthyl)ethyl)-1-aza-4,8-dithiacyclodecane)} (**5**) has been shown to coordinate the double bond adjacent to the ethylene bridge of the pendant naphthyl moiety [54–56]. Two Pt(0) complexes have also been reported with fluorinated aromatic ligands. Crystal structures of $[\eta^2\text{-}C_6(CF_3)_6]Pt(PEt)_3$ (**3**) and $\{\eta^2\text{-}C_6[1,2\text{-}3,4\text{-}5,6\text{-}(C_2F_4)_3]\}Pt(PPh_3)_2$ (**4**) have been reported with C–C bond lengths of around 1.51 Å [57,58].

Of more direct interest are the d^{10} systems of Ni(0). In 1977 Brauer and Krüger reported the crystal structure of the dihapto anthracene complex $[(C_6H_{11})_3P]_2Ni(\eta^2\text{-}C_{14}H_{10})$ (**6a**) [59]. This complex shows carbon–carbon bond lengths that are quite different from those observed in the free aromatic as a result of partial localization of electrons in the bound ring. The analogous complexes of $P(Bu)_3$ and $P(Et)_3$ (**6b**,**c**) have also been characterized by X-ray crystallography [60]. A solid-state structure of a nickel(0) complex of naphthalene has been described in which the ligand set contains the chelating ligand bis(diisopropylphosphino)ethane (**7**) [61]. Modification

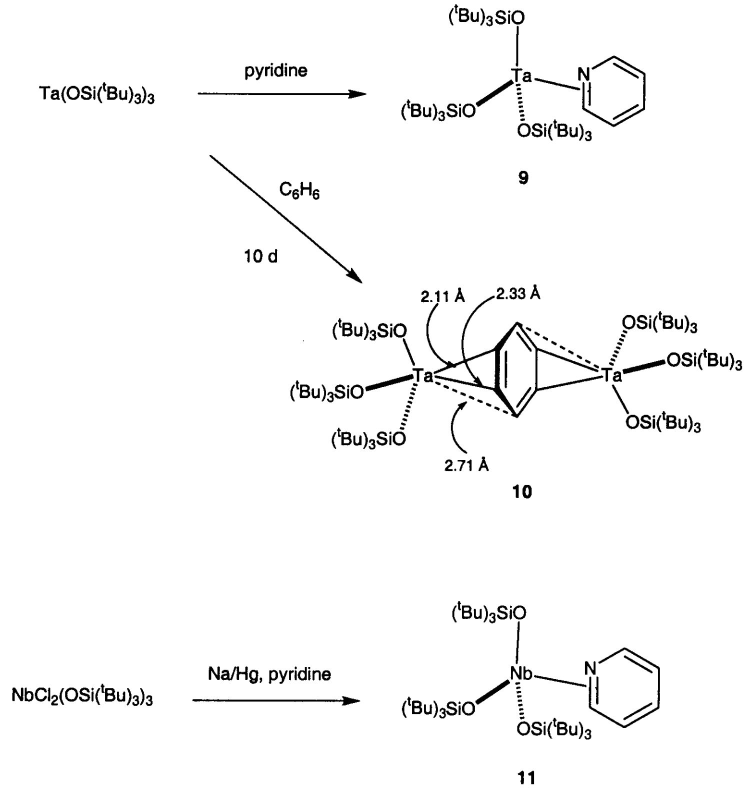


Scheme 19.

of the chelate to the 1,2-bis(diethylphosphino)ethane (depe) ligand affords an example of an η^3- and η^4-coordinated anthracene species in a single crystal structure for the (depe)Ni($C_{14}H_{10}$) complex (**8**) [62]. The η^3 complex is thought to be evidence for an intermediate in the conversion between the η^2 and η^4 isomers.

3.1.2. d^2 Systems of tantalum(III) and niobium(III)

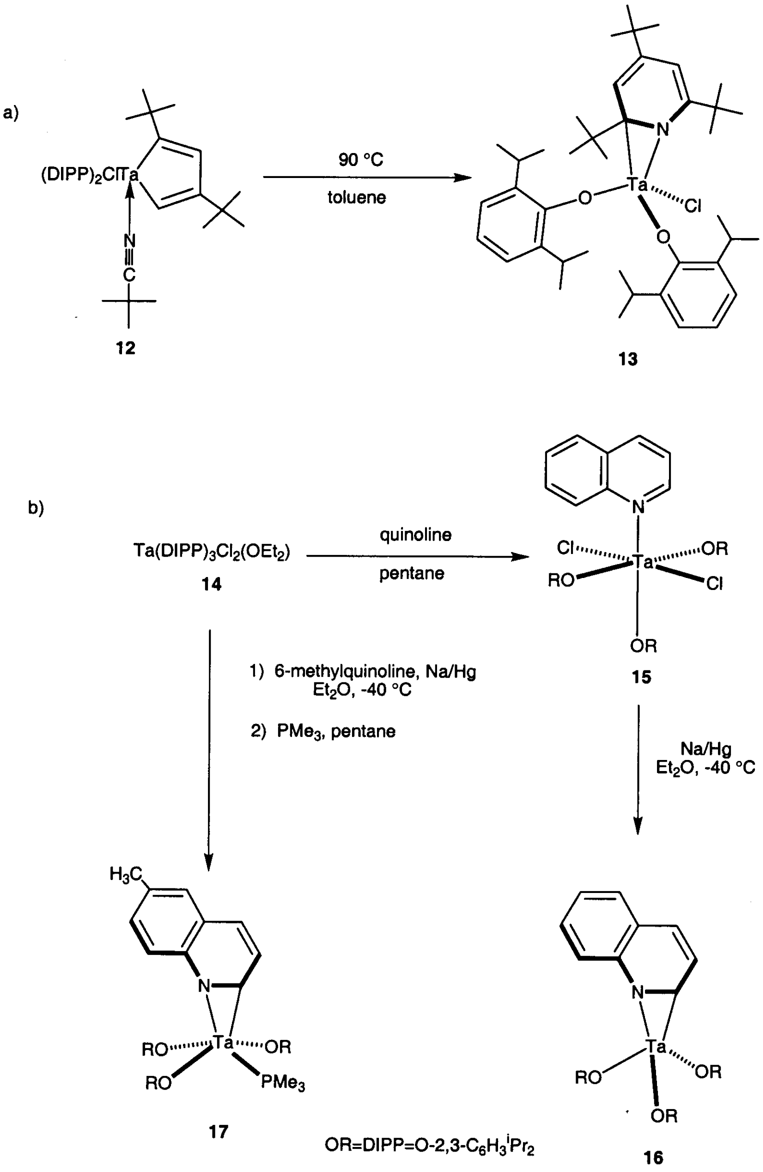
Wolczanski et al. have utilized the silox (^{t}Bu$_3$SiO$^-$) ligand to synthesize the dihapto complex of pyridine (silox)$_3$Ta(η^2-(*N*,*C*)-C_5H_5N) (**9**) (Scheme 20). Besides being an early example of a dihapto-coordinated aromatic heterocycle, this complex



Scheme 20.

also represents a rare instance of an *N*,*C*-bound pyridine. When Ta(silox)$_3$ is allowed to stand in benzene solution for more than 10 days, the proposed bimetallic complex [(silox)$_3$Ta]$_2${μ-η^2(1,2):η^2(4,5)-C_6H_6} (**10**) is formed. Though the crystal structure of complex **10** exhibits Ta–C bond lengths within expected limits, the distance between the tantalum and the carbon adjacent to one of the bound carbons of 2.71 Å cannot discount a bis-allyl bonding description [63]. The niobium analog of the pyridine complex (silox)$_3$Nb(η^2-(*N*,*C*)-C_5H_5N) (**11**) has been prepared by reduction of Nb(silox)$_3$Cl$_2$ with Na/Hg in pyridine [64].

Wigley et al. have developed Ta systems with the DIPP (2,6-diisopropylphenoxide or *O*-2,6-$C_6H_3^iPr_2$) ligand that also display η^2-(*N*,*C*) coordination of pyridine derivatives. The metallacyclopentadiene complex **12** (Scheme 21) has been shown to undergo a [2 + 2 + 2] cycloaddition with ^{t}BuCN to form the dihapto complex (η^2-(*N*,*C*)-2,4,6-$NC_5H_2^tBu_3$)Ta(DIPP)Cl (**13**) [65]. Similarly, the η^2-(*N*,*C*) quinoline and 6-methylquinoline complexes (**16** and **17**) can be formed from the Ta(V) precursor Ta(DIPP)$_3$(Cl)$_2$(OEt$_2$) (**14**) [66]. The η^2-quinoline complex **16** is formed



Scheme 21.

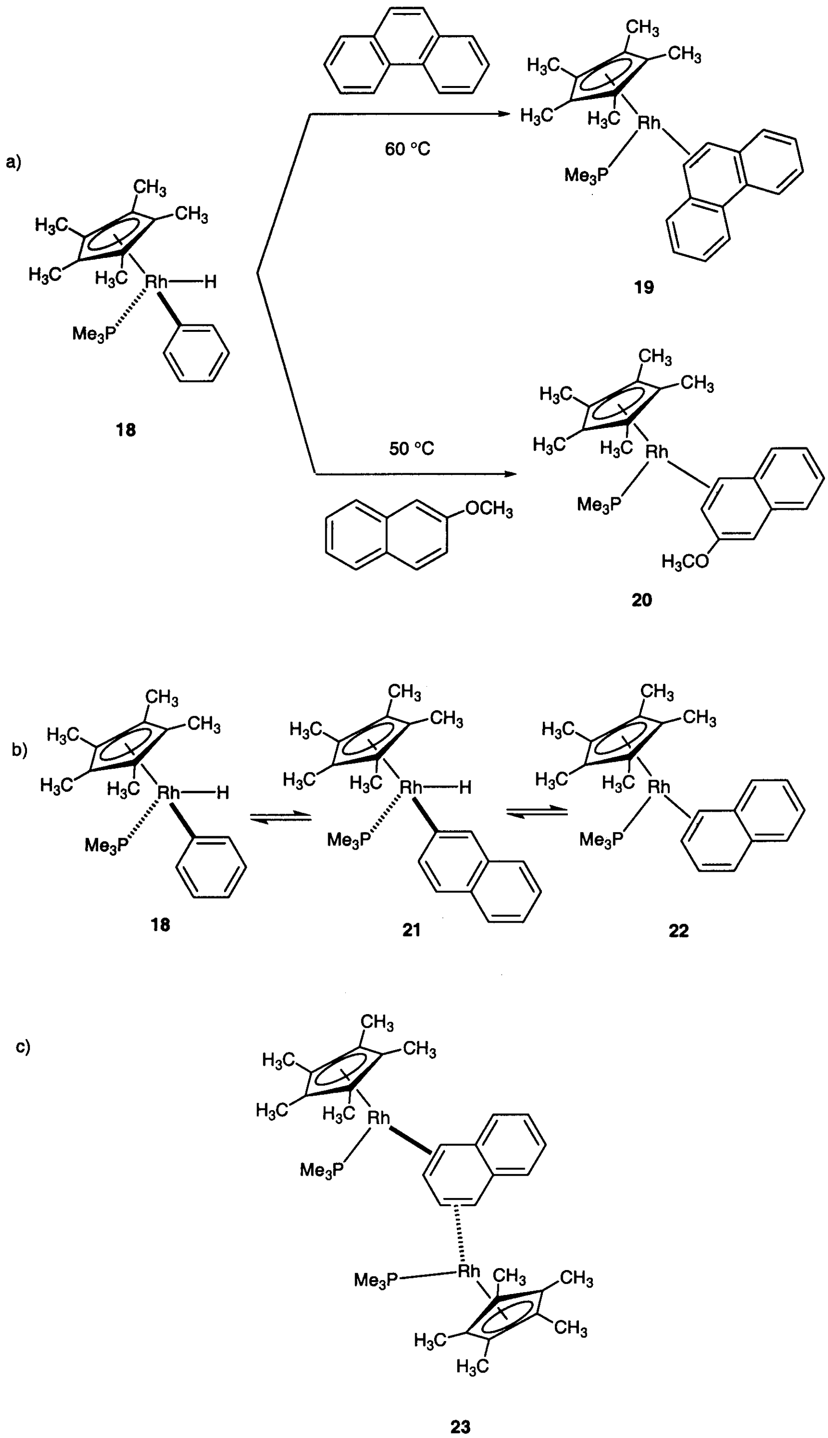
by η^1 to η^2 conversion of the octahedral complex (η^1-(*N*)-quinoline)Ta(Cl)$_2$(DIPP)$_3$ (**15**). In the latter Ta systems, the authors suggest that the metal centers are more accurately described as Ta(V) metallaaziridine complexes based on structural and PES data.

3.1.3. d^8 Systems of rhodium(I) and ruthenium(0)

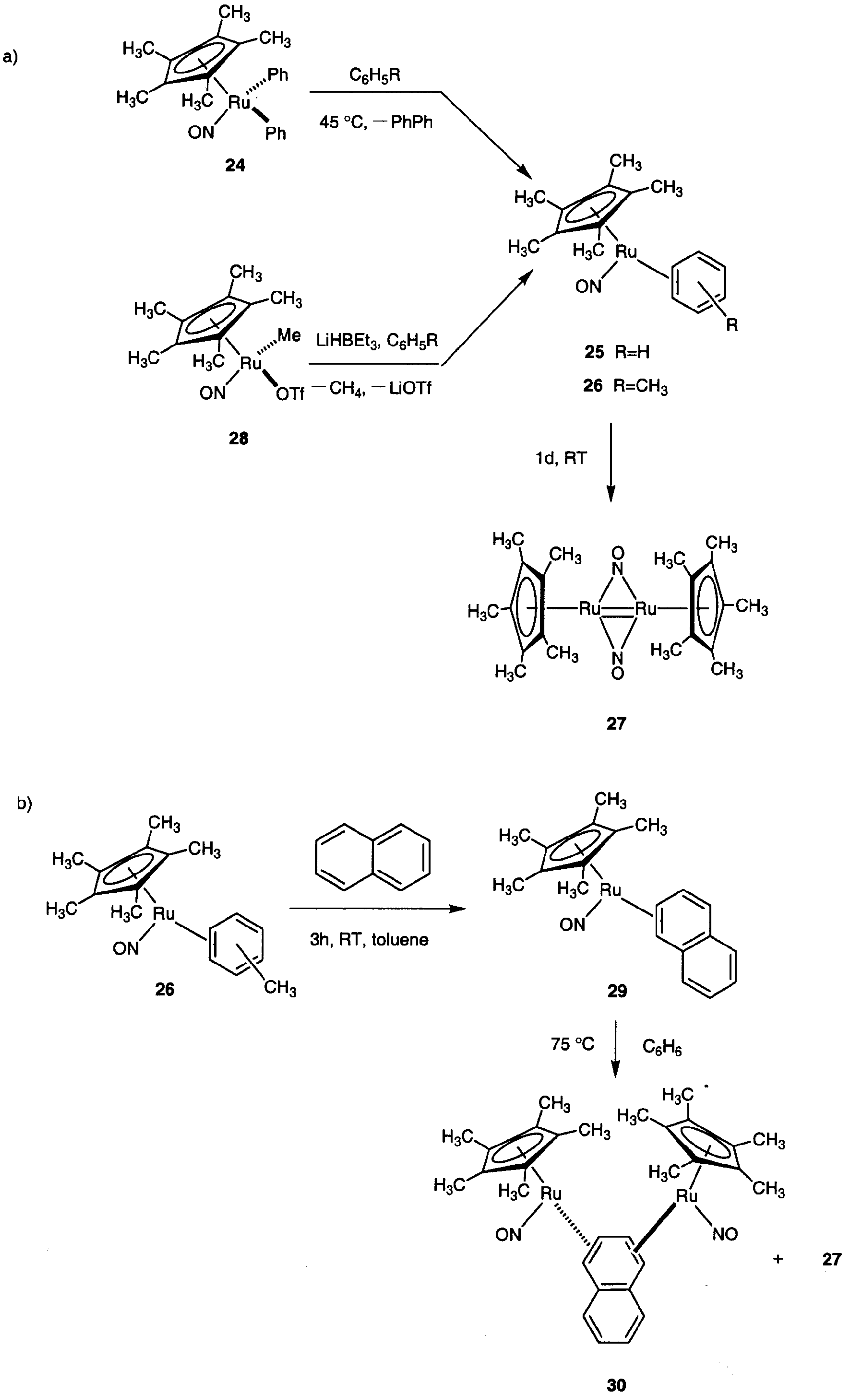
Perhaps the most pertinent examples of dihapto complexes of aromatic molecules have come within the last 15–20 years. The rhodium-pentamethylcyclopentadienyl (Cp*) system described by Jones et al. forms stable η^2-coordinated complexes of the form Cp*Rh(PMe_3)(η^2-arene) for phenanthrene, naphthalene, and 2-methoxynaphthalene at r.t. (Scheme 22) [67]. Data for the existence of the metastable η^2-coordinated complexes of toluene and benzene have been reported. Strong evidence for the existence of Cp*Rh(PMe_3)(η^2-toluene) was established as early as 1982 [68]. The putative toluene complex has been postulated as an intermediate between the rapidly interconverting *meta* and *para*-tolyl hydrides. More direct evidence for an η^2-benzene intermediate has been obtained by following the analogous conversion of the deuterated phenyl complex Cp*Rh(PMe_3)(C_6D_5)(H) by ^{1}H-NMR spectroscopy [69,70].

The phenanthrene, naphthalene and 2-methoxynaphthalene complexes have been synthesized from the phenyl hydride complex Cp*Rh(PMe_3)(Ph)(H) (**18**), which loses benzene upon heating in hexane. The dihapto-coordinated complexes Cp*Rh(PMe_3)(9,10-η^2-phenanthrene) (**19**) and Cp*Rh(PMe_3)(3,4-η^2-(2-methoxynaphthalene)) (**20**) are the only species observed for the complexation of these aromatic hydrocarbons. The naphthalene complex Cp*Rh(PMe_3)(1,2-η^2-naphthalene) (**22**) has been found to be in equilibrium with the naphthyl hydride complex Cp*Rh(PMe_3)($C_{10}H_7$)(H) (**21**) and phenyl hydride precursor when heated for 24 h in a 10:10:1 solution of benzene, naphthalene and **18**. The equilibrium ratio of **18**, **21** and **22** has been found to be 1:1.35:2.7. Heating for longer periods (2 weeks) yields an additional product which has been characterized by ^{1}H-NMR spectroscopy and X-ray crystallography as the bimetallic complex [Cp*Rh(PMe_3)$]_2$(1,2-η^2-3,4-η^2-naphthalene) (**23**) [71].

A recent report from Bergman's laboratory details the chemistry of an electron-rich coordinatively unsaturated Ru(0) system (Scheme 23) [72]. When heated in aromatic solvents, the complex Cp*Ru(NO)$(Ph)_2$ (**24**) eliminates the phenyl ligands to give η^2-coordinated complexes of the form Cp*Ru(NO)(η^2-arene). The benzene and toluene complexes Cp*Ru(NO)(η^2-benzene) (**25**) and Cp*Ru(NO)(η^2-toluene) (**26**) are both synthesized in this manner. A more favorable route to complexes **25** and **26** involves reaction of Cp*Ru(NO)(Me)(OTf) (**28**) with $LiHBEt_3$ in the aromatic solvent. The dihapto-coordinated naphthalene complex Cp*Ru(NO)(1,2-η^2-naphthalene) (**29**) is also formed by stirring the toluene complex with naphthalene in toluene solution at r.t. The 9,10-η^2-phenanthrene complex is synthesized either from the toluene complex **26** or the naphthalene complex **29**. The benzene and toluene complexes are kinetically and thermally unstable and form the bis(nitrosyl) dimer [Cp*Ru(μ-NO)$]_2$ (**27**) after 1 day in solution at r.t. In contrast, it is necessary to heat the naphthalene complex **29** to approximately 75°C in order to see degradation. One product of this degradation has been characterized by ^{1}H-NMR spectroscopy as the bimetallic complex [Cp*Ru(NO)$]_2$(1,2-η^2-3,4-η^2-naphthalene) (**30**) while the bridged bis(nitrosyl) dimer **27** is also produced. Nevertheless, the benzene and naphthalene complexes **25** and **29** exhibit fluxional behavior in the ^{1}H-NMR spectra at r.t. PSEXSY studies with **29** have revealed that the fluxional



Scheme 22.


a)
24
C_6H_5R
45 °C, − PhPh
28
$LiHBEt_3$, C_6H_5R
− CH_4, − LiOTf
Me
OTf
Ph
ON
Ru
R
25 R=H
26 R=CH_3
1d, RT
27
b)
26
3h, RT, toluene
29
75 °C
C_6H_6
NO
30
+ 27

Scheme 23.

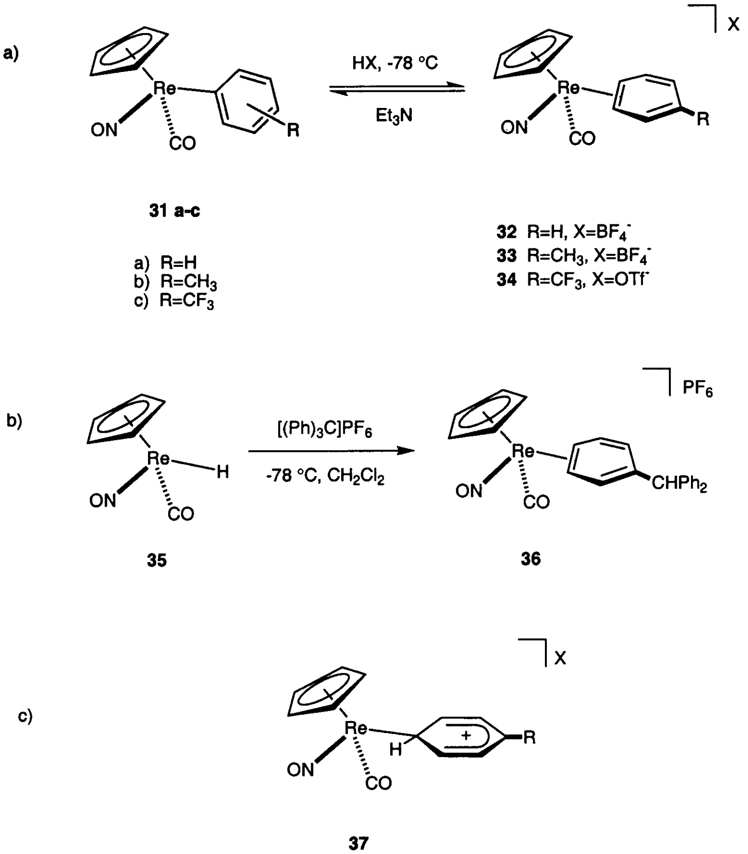
process is due to movement of the metal from the coordinated double bond to the uncoordinated double bond of the same ring. Interestingly, the bimetallic naphthalene species **30** is similar in structure to the bimetallic benzene complex $[CpRe(CO)_2]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-benzene})$ that has been described by Orpen et al. [73], the Os(II)/M(II) naphthalene complexes reported by Harman et al. [18,74] of the form $[Os(NH_3)_5M(NH_3)_5(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-naphthalene})]^{4+}$ (M = Os, Ru), and the Rh(I) system $[Cp^*Rh(PMe_3)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-naphthalene})$ detailed by Jones et al. [71](vide supra). Although the thermal stability of these arene complexes is unusually high, recent experiments carried out in our laboratories indicate that these Ru(0) systems are intolerant of protic solvents (e.g. alcohols) and are thus unlikely to tolerate electrophilic reagents.

3.1.4. d^6 Systems of ruthenium(II) and rhenium(I)

The pentaammineruthenium(II) system has been shown to bind aromatic ligands in a dihapto fashion much like the pentaammineosmium(II) system; however, the ruthenium(II) system tends to form bimetallic species with ligands such as benzene and naphthalene [18]. Presumably, this is due to the electron-deficient nature of the ruthenium(II) relative to the osmium(II) system. Another ruthenium(II) system has been shown to bind the aromatic heterocycle pyrazine in a dihapto-fashion. Thus, the complex $[Ru(hedta)(pz)]^-$(pz = pyrazine and hedta = *N*-(hydroxyethyl)-ethylenediaminetriacetate) has been shown to exhibit fluxional N1 to N4 conversion at r.t. In addition, the protonated form of this complex contains a 63:20:16 ratio of $1,2\text{-}\eta^2$-, $2,3\text{-}\eta^2$- and N1-bound isomers, respectively [75]. The relative amounts of these isomers for the pyrazinium system have been deduced from ^1H-NMR data.

Apart from the osmium(II) system, the metal which has been shown to be the most amenable to binding aromatic molecules in a dihapto-fashion is rhenium(I). Graham and Sweet have reported evidence for the formation of a dihapto complex with the rhenium-cyclopentadienyl (Cp) fragment $\{CpRe(CO)(NO)\}^+$ (Scheme 24) [76]. Protonation of the appropriate aryl complexes (**31a**–**c**) at −78°C with HBF_4 or HOTf affords the η^2-arene complexes $[CpRe(CO)(NO)(\eta^2\text{-benzene})][BF_4]$ (**32**), $[CpRe(CO)(NO)(\eta^2\text{-toluene})][BF_4]$ (**33**), and $[CpRe(CO)(NO)(\eta^2\text{-trifluoromethylbenzene})][OTf]$ (**34**). Addition of triphenylcarbenium hexafluorophosphate to CpRe(CO)(NO)(H) (**35**) in methylene chloride at −78°C also yields the complex $[CpRe(CO)(NO)(\eta^2\text{-}C_6H_6CHPh_2)][PF_6]$ (**36**) [77]. The ^1H-NMR spectra of these species are consistent with dihapto coordination due to upfield shifts for the resonances of the bound protons and the lack of any hydridic proton signals. The fluxionality of the ^1H-NMR spectra for complexes **32**–**34**, **36** has been postulated to be caused by migration of the rhenium center around the ring via an η^1-arenium intermediate **37**. All of the complexes reported quickly decompose in solution at temperatures above −40°C.

Another rhenium(I) system which has been shown to coordinate aromatic molecules in a dihapto-fashion is the $\{Cp^*Re(CO)_2\}$ fragment. Orpen et al. have reported the reaction and solid-state structure of the bimetallic $[Cp^*Re(CO)]_2(1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-benzene})$ (**42**) (Scheme 25) [73]. The benzene-bridged system has been

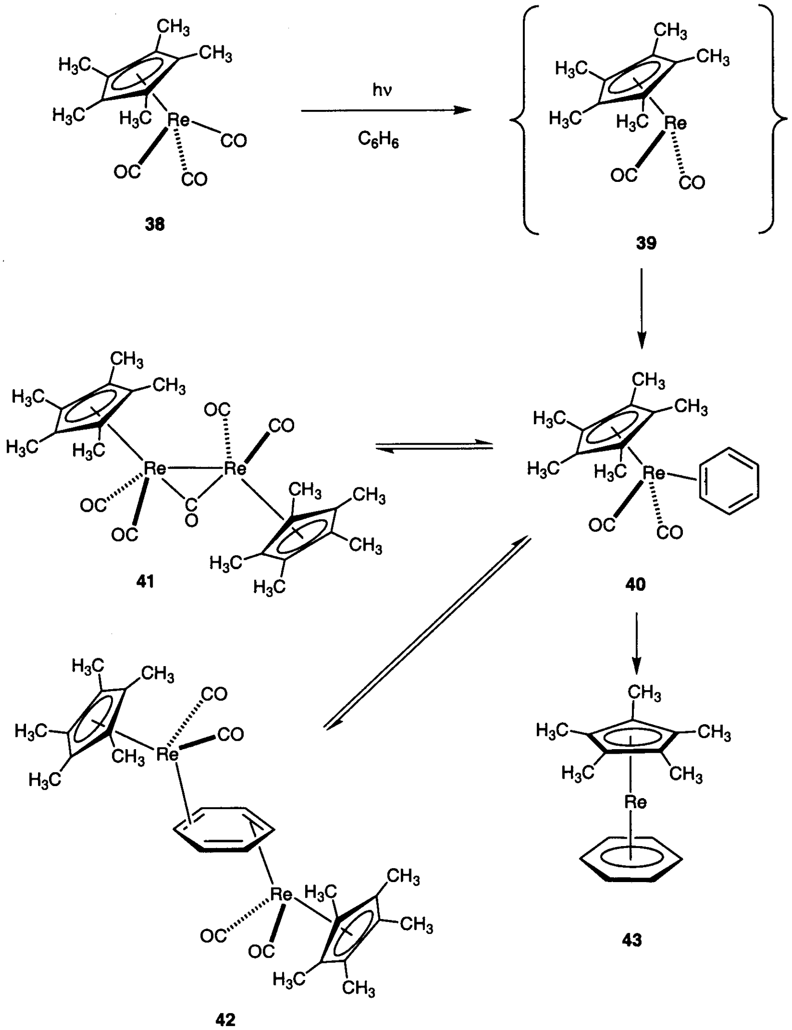


Scheme 24.

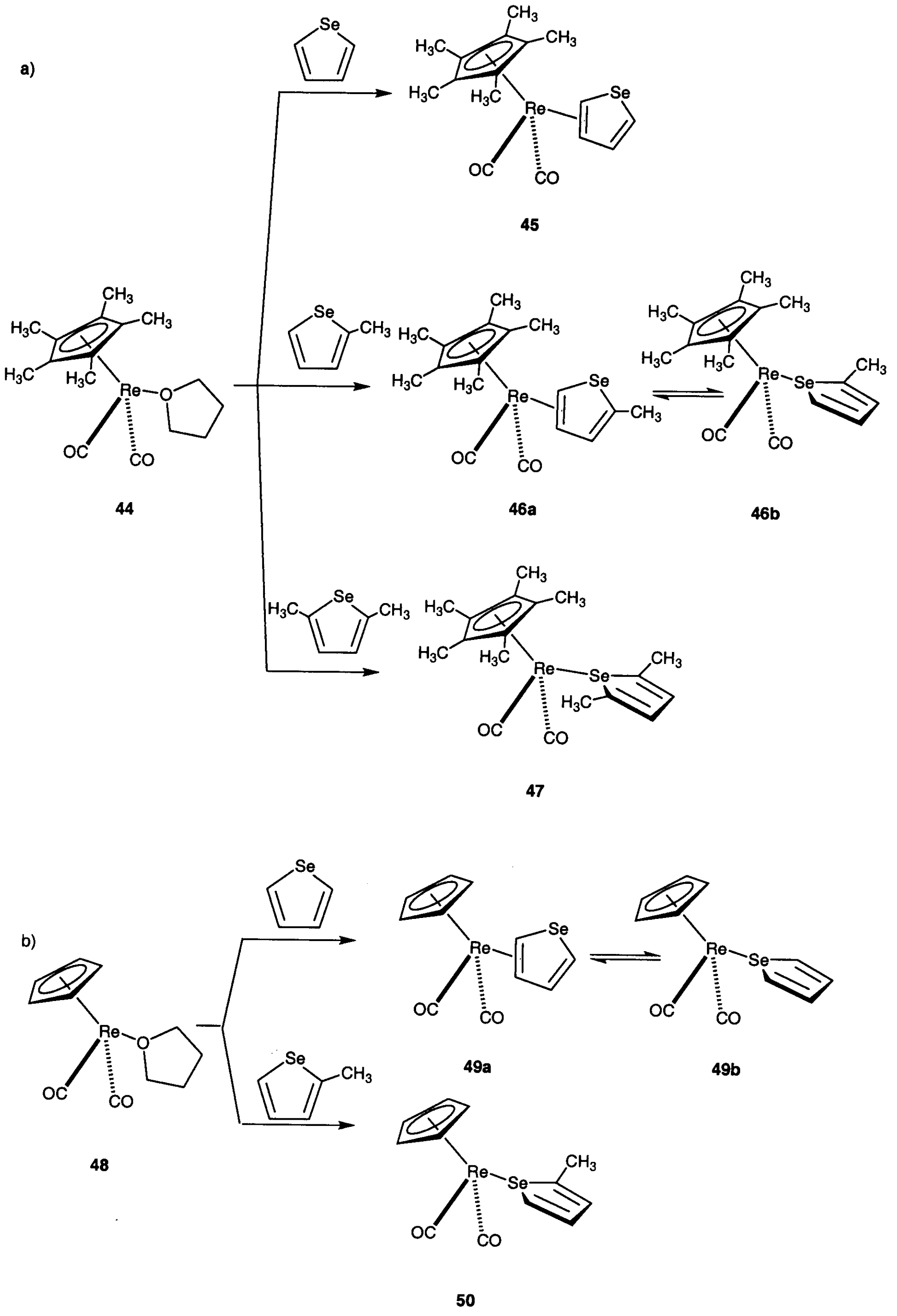
synthesized in low yield by photolysis of the tricarbonyl precursor Cp*Re(CO)$_3$ (**38**) in benzene. In addition to the bimetallic complex **42**, the CO-bridged species [Cp*Re(CO)$_2$]$_2$(μ-CO) (**41**) and sandwich complex Cp*Re(η^6-benzene) (**43**) have been isolated after photolysis and work-up. Complex **41** is not a direct product of photolysis, but rather is proposed to be a degradation product formed by the loss of benzene from the monomeric intermediate Cp*Re(CO)$_2$(η^2-benzene) (**40**). Accordingly, immediate analysis of the photo-products of the reaction has revealed that only the mononuclear **40** and the sandwich complex **43** are present. Benzene is coordinated to the 16-electron intermediate {Cp*Re(CO)$_2$} (**39**) following photolytic removal of CO from the starting material. Reversible loss of benzene from the mononuclear benzene complex **40** then gives the bimetallic species **42** and **41** while further photolysis affords the sandwich complex **43**.

Angelici et al. have also utilized the {Cp*Re(CO)$_2$} fragment to coordinate selenophene and benzothiophene in an η^2-fashion. These complexes represent rare examples of dihapto-coordinated complexes of aromatic heterocycles. The complex

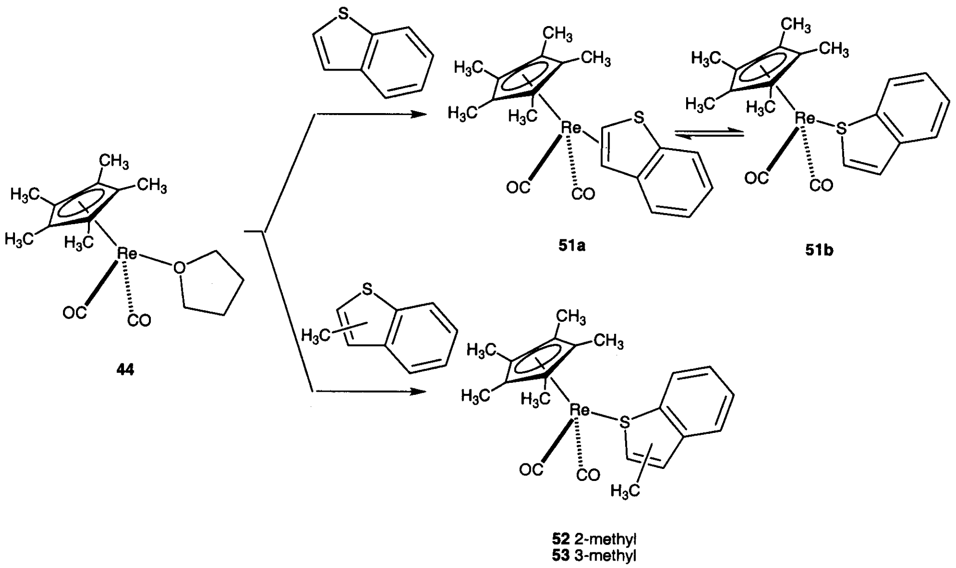
$Cp^{*}Re(CO)_2(2,3\text{-}\eta^2\text{-selenophene})$ (**45**) (Scheme 26) has been prepared from the tetrahydrofuran (THF) complex $Cp^{*}Re(CO)_2(THF)$ (**44**) by stirring in selenophene for 7 h. Interestingly, the analogous reaction with thiophene yields only the *S*-bound isomer [78]. Spin saturation experiments have confirmed the rapid interconversion of the 2,3-η^2 and 4,5-η^2 isomers of the selenophene complex [79]. The authors have suggested that this equilibrium proceeds through the *Se*-bound isomer. Further support for this proposal has been obtained from the analogous reaction of **44** with 2,5-dimethylselenophene which yields only the *Se*-bound species $Cp^{*}Re(CO)_2(\eta^1\text{-}(Se)\text{-}2,5\text{-dimethylselenophene})$ (**47**). The reaction with 2-methylselenophene affords a mixture of the two *Se*-bound and η^2-bound isomers **46a**,**b** [79].



Scheme 25.



Scheme 26.

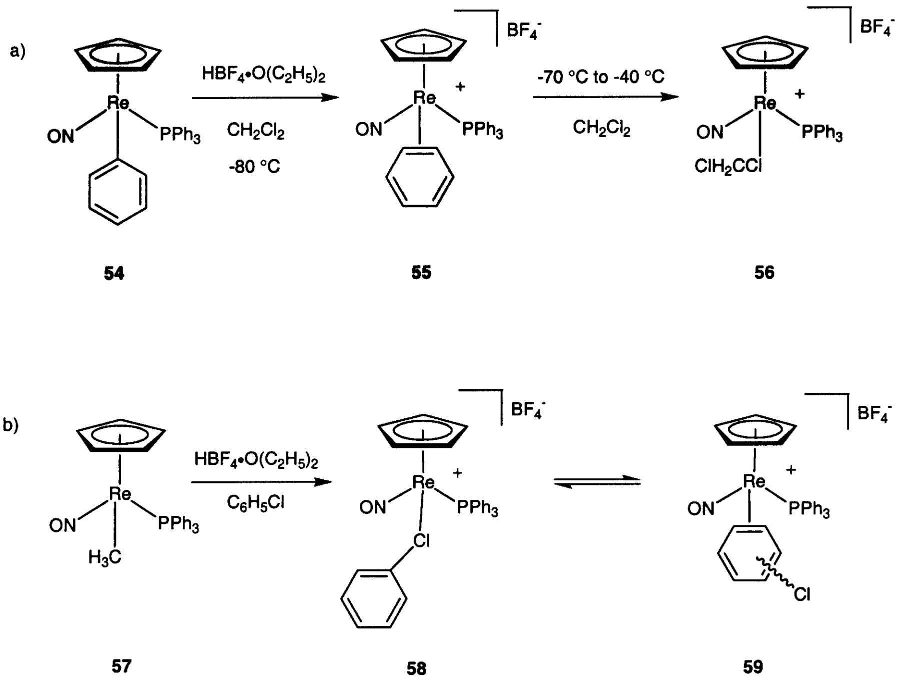


Scheme 27.

In addition, the analogous cyclopentadienyl system $\{CpRe(CO)_2\}$ produces a mixture of η^1 and η^2 isomers for the parent selenophene **49a**,**b**. The *Se*-bound isomer $CpRe(CO)_2(\eta^1$-(*Se*)-selenophene) (**49b**) is favored by 3:1 (r.t.) over the η^2-coordinated species **49a**. Only the monohapto-coordinated species has been observed for the 2-methylselenophene complex $CpRe(CO)_2(\eta^1$-(*Se*)-2-methylselenophene) (**50**). The differences in monohapto and dihapto coordination exhibited by the Cp and Cp* systems for the selenophene complexes have been explained by the greater donating ability of the latter which causes the metal to become a better π-donor.

The coordination of benzothiophene (Scheme 27) has also been observed to be in rapid equilibrium between the 2,3-η^2 and *S*-bound species for the $\{Cp^*Re(CO)_2\}$ fragment [80] The ratio of $Cp^*Re(CO)_2(2,3$-η^2-benzothiophene) (**51a**) to $Cp^*Re(CO)_2(\eta^1$-(*S*)-benzothiophene) (**51b**) is 1.6:1 (r.t.). Again, complexation of the 2-methyl and 3-methyl derivatives of the heterocycle gives only the *S*-bound isomers $Cp^*Re(CO)_2(\eta^1$-(*S*)-2-methylbenzothiophene) (**52**) and $Cp^*Re(CO)_2(\eta^1$-(*S*)-3-methylbenzothiophene) (**53**) [80].

Gladysz et al. have demonstrated the existence of a fluxional η^2-coordinated benzene complex of the Re(I) fragment $\{CpRe(NO)(PPh_3)\}^+$ (Scheme 28). Protonation of the corresponding phenyl complex $[CpRe(NO)(PPh_3)(Ph)]$ (**54**) with $HBF_4 \cdot OEt_2$ at $-80°C$ in CH_2Cl_2 yields the dihapto-coordinated complex $[CpRe(NO)(PPh_3)(\eta^2\text{-benzene})][BF_4]$ (**55**) [81]. Warming the solution to $-70°C$ produces the methylene chloride complex (**56**). The ^1H- and ^{13}C-NMR spectra of complex **55** contain signals at 6.49 and 109 ppm, respectively, consistent with a fluxional benzene species. The η^2-coordinated benzene complex also contains a distinct resonance in the ^{31}P-NMR spectrum at 8.1 ppm. Evidence has also been



Scheme 28.

found for the same system coordinating chlorobenzene in an η^2-fashion. The dihapto-bound isomer $[CpRe(NO)(PPh_3)(\eta^2\text{-chlorobenzene})]^+$ (**59**) is believed to be in equilibrium with the Cl-bound η^1 species (**58**) at -44°C [82]. Complex **59** is produced from the methyl complex $CpRe(NO)(PPh_3)(CH_3)$ (**57**). The large number of possible isomers for **59** greatly complicates the characterization of the complex by ^1H-NMR; however, the ^{31}P spectrum exhibits a resonance at 5.5 ppm which is consistent with that observed for $[CpRe(NO)(PPh_3)(\eta^2\text{-benzene})]^+$ (**55**).

Thus, while there are a variety of other systems that coordinate aromatic molecules in an η^2-fashion, the pentaammineosmium(II) system is unique. The $\{Os(NH_3)_5\}^{2+}$ fragment differs from the systems listed above in several important ways. Of paramount importance in relation to the organic transformations performed with the pentaammineosmium(II) moiety is the fact that this fragment forms thermally stable complexes with a wide variety of arenes and aromatic heterocycles. Perhaps more importantly, the electron-rich osmium system does not suffer from oxidative addition. Accordingly, efforts in our laboratory focused on developing ligand sets for rhenium(I) systems that would not only form thermally stable η^2-coordinated complexes with arenes, but also would deter the competing oxidative addition pathway.

3.2. Pentaaminerhenium(III/II) and rhenium-pyridyl systems

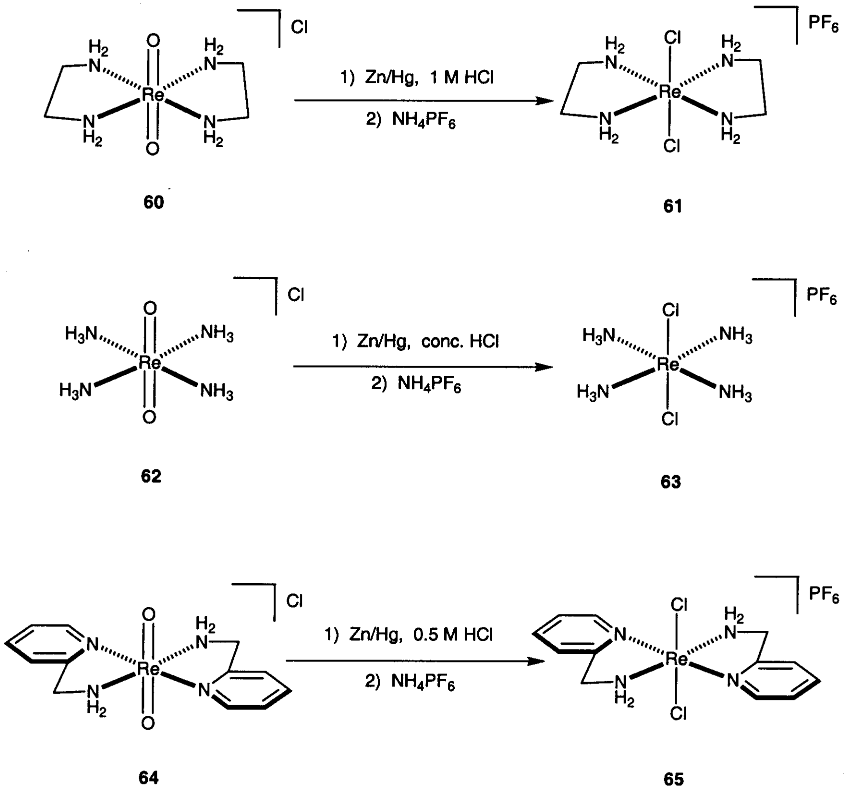
Rhenium(I) was chosen initially because of the relatively low cost of perrhenic acid (this rhenium starting material is roughly 1/12 the cost per gram of osmium tetroxide). Perrhenic acid is easier to handle and less dangerous than OsO_4 since this Re precursor is sold as an aqueous solution. Rhenium(I) is also expected to be intrinsically more electron-rich than osmium(II) due to the lower oxidation state of the former. Indeed, the observation of dihapto-coordination of several aromatic ligands by relatively electron deficient systems of rhenium (vide supra) seemed to indicate a more electron-rich d^6 rhenium system would be a tenacious π back-bonding agent. Thus, while an abundance of reports of low valent rhenium complexes containing π-acid ligands exist [83,84], there was a paucity of rhenium complexes in low oxidation states with σ-donor ligands such as amines or phosphites [85,86]. Accordingly, early synthetic attempts in our laboratory focused on the development of rhenium(I) fragments with primarily saturated amine, phosphine or pyridyl ligands which coordinated unsaturated organic moieties in an η^2-fashion. The evolution of these systems and the initial evidence for a class of practical rhenium dearomatization agents are presented in the following sections.

3.2.1. Pentaaminerhenium(III/II) complexes

The basic approach for development of rhenium(I) dearomatization agents initially involved a process that paralleled the synthesis of the Os(III) precursor $[Os(NH_3)_5(OTf)][OTf]_2$ [15,87,88]. This strategy involved the reduction of high valent rhenium complexes to low-valent species with the addition of saturated amines, phosphines or pyridines at each step.

The synthesis of rhenium(V) oxo complexes (Scheme 29) of the type *trans*-$[Re(L)_4(O)_2]^+$ {L = 1/2(en) (**60**), NH_3 (**62**), PPh_3} has been reported previously [89,90] from the complex $Re(O)Cl_3(PPh_3)_2$,which is produced in high yield from $HReO_4$ by addition of HCl and PPh_3 in acetic acid [91]. In addition, the analogous 2-(aminomethyl)pyridine (ampy) complex *trans*-$[Re(ampy)_2(O)_2]Cl$ (**64**) has been synthesized in our laboratory by addition of ampy and water to an acetone solution of $Re(O)Cl_3(PPh_3)_2$ [92]. The reduction of these oxo complexes with Zn/Hg in HCl gives the analogous Re(III) bis(chloride) complexes *trans*-$[ReCl_2(L)_4]PF_6$ {L = 1/2(en) (**61**), NH_3 (**63**), and 1/2(ampy) (**65**)} after precipitation from the aqueous solution with NH_4PF_6. The isolated yield for complex **61** is good (79%) while the yields for the **63** and **65** systems are lower (31 and 36%, respectively).

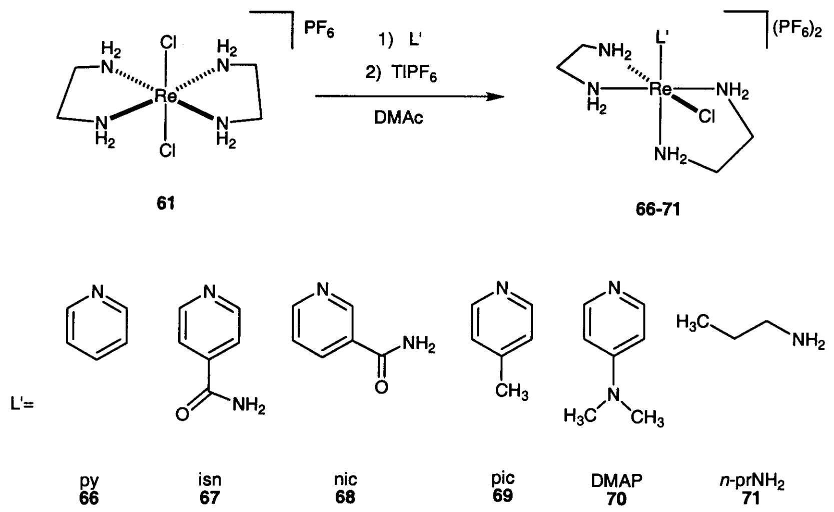
Addition of another amine or pyridyl ligand and $TlPF_6$ to the complex *trans*-$[ReCl_2(en)_2]PF_6$ in DMAc affords a variety of pentaaminerhenium(III) complexes of the type *cis*-$[Re(Cl)(L')(en)_2][PF_6]_2$ where L′ = pyridine (py, **66**, 21%), isonicotinamide (isn, **67**, 65%), nicotinamide (nic, **68**, 89%), 4-picoline (pic, **69**, 76%), 4-(dimethylamino)pyridine (DMAP, **70**, 39%) and *n*-propylamine (*n*-$prNH_2$, **71**) (Scheme 30). The isolation of the *n*-propylamine complex is hampered by the presence of starting material and decomposition for longer reaction times. The trans isomers of the pyridine and DMAP complexes have also been obtained by stirring the appropriate cis complexes in MeOH for 4 days. This isomerization is



Scheme 29.

postulated to be the result of a thermodynamically favored process due to the insolubility of the trans isomers in MeOH.

Electrochemical data have provided a wealth of information about the electronic characteristics of many of the rhenium systems that have been synthesized by providing a reliable comparison to various pentaammineosmium(II) systems. The cyclic voltammogram of *trans*-$[ReCl_2(en)_2]PF_6$ (**61**) in DMAc exhibits a chemically irreversible anodic peak at 0.18 V (vs. NHE) as well as an irreversible two-electron cathodic peak at -1.88 V (scan rate 100 mV s^{-1}). The oxidation wave becomes reversible in CH_3CN and is shifted to 0.42 V. The ammine complex *trans*-$[ReCl_2(NH_3)_4]PF_6$ (**63**) also contains a two-electron wave (-1.84 V) like the analogous bis(ethylenediamine) system. In contrast, the bis(ampy) complex (**65**) exhibits separate III/II and II/I couples at -1.15 and -2.01 V, respectively, in DMAc. The monochloride complexes **66**–**71** have similar voltammograms in DMAc and CH_3CN except that separate III/II and II/I couples are observed. The exception to this observation is the *n*-propylamine complex *cis*-[Re(Cl)(*n*-$prNH_2)(en)_2][PF_6]_2$ (**71**), which contains a two-electron reduction wave at -1.73 V. The chemical instability of the Re(II) analog of the pentaamine species is demon-



Scheme 30.

strated by the fact that the reversible II/I couples become irreversible at slower scan rates or by holding the potential at a more negative value than the reduction potential. A summary of the electrochemical data for the Re(III) complexes is listed in Table 1.

Furthermore, comparison of electrochemical data to the pentaammineosmium(II) and ruthenium(II) systems reveals that the rhenium system in the 2+ oxidation state (e.g. the fragment $\{Re(en)_2Cl\}^+$) has a higher affinity for electron-withdraw-

Table 1
Cyclic voltammetric data for several Re(III) cations[a]

Complex	Re IV/III $E_{p,a}$ (V)	Re III/II $E_{1/2}$ (V)	Re II/I $E_{p,c}$ (V)
$[ReCl(isn)(en)_2]^{2+}$ (**67**)	0.76	-0.93^b	-2.11
$[ReCl(nic)(en)_2]^{2+}$ (**68**)	0.65	-1.10^b	-1.98
$[ReCl(py)(en)_2]^{2+}$ (**66**)	0.64	-1.14^b	-2.14
$[ReCl(pic)(en)_2]^{2+}$ (**69**)	0.60	-1.24^b	-2.24
$[ReCl(DMAP)(en)_2]^{2+}$ (**70**)	0.42	-1.44^b	d
$[ReCl(n\text{-}prNH_2)(en)_2]^{2+}$ (**71**)	0.44	-1.73^c	
$[ReCl_2(en)_2]^+$ (**61**)	0.18	-1.88^c	
$[ReCl_2(ampy)_2]^+$ (**65**)	0.53	-1.15^b	-2.01
$[ReCl_2(NH_3)_4]^+$ (**63**)	0.34^b	-1.84	

[a] Note: All scans recorded in DMAc; values reported vs. NHE.
[b] Reversible couple; ($E_{1/2}$).
[c] A two-electron wave.
[d] Not observed; $E_{p,c} < -2.3$V.

Table 2
Equilibrium data for the generalized reaction: $L_nM–L_A + L_B = L_nM–L_B + L_A$

L_nM	L_A	L_B	K_{eq}	Ref.
$\{Ru(NH_3)_5\}^{2+}$	H_2O	Cl^-	1.6^a	[93]
$\{Ru(NH_3)_5\}^{2+}$	H_2O	py	2.5×10^{7a}	[94]
$\{Ru(NH_3)_5\}^{2+}$	H_2O	isn	3.0×10^{8a}	[94]
$\{Ru(NH_3)_5\}^{2+}$	py	isn	1.2×10^{1}	c
$\{Ru(NH_3)_5\}^{2+}$	py	Cl^-	6.4×10^{-8}	c
$\{Ru(NH_3)_5\}^{3+}$	H_2O	Cl^-	1.0×10^{2a}	[93]
$\{Ru(NH_3)_5\}^{3+}$	H_2O	py	3×10^{3a}	[94]
$\{Ru(NH_3)_5\}^{3+}$	H_2O	isn	1.8×10^{3a}	[94]
$\{Ru(NH_3)_5\}^{3+}$	py	isn	6.0×10^{-1}	c
$\{Ru(NH_3)_5\}^{3+}$	py	Cl^-	3.5×10^{-2}	c
$\{Os(NH_3)_5\}^{3+}$	py	isn	~1	d
$\{Os(NH_3)_5\}^{2+}$	py	isn	$\sim2.5\times10^{2}$	[92]
$\{Re(en)_2Cl\}^{2+}$	py	isn	6.3×10^{-1a}	[92]
$\{Re(en)_2Cl\}^{2+}$	nic	isn	~1	[92]
$\{Re(en)_2Cl\}^{2+}$	py	Cl^-	1.4×10^{2b}	[92]
$\{Re(en)_2Cl\}^{+}$	py	isn	2.2×10^{3b}	[92]
$\{Re(en)_2Cl\}^{+}$	nic	isn	7.5×10^{2b}	[92]
$\{Re(en)_2Cl\}^{+}$	py	Cl^-	$<4\times10^{-11b}$	[92]

[a] Reported for aqueous solution where the activity of water is unity.

[b] Value reported for DMAc solution.

[c] See text.

[d] Estimated value.

ing ligands (Table 2) [93,94]. Thus, the K_{eq} for substitution of the π-acidic pyridine ligand for Cl^- is 6.4×10^{-8} for $\{Ru(NH_3)_5\}^{2+}$ while the upper limit for the $\{Re(en)_2Cl\}^{+}$ fragment is 4×10^{-11}. The analogous value for the pentaammineosmium(II) system has not been measured, but is expected to be comparable ($\sim10^{-9}$) to the ruthenium system. A more direct illustration of the electron-rich nature of the rhenium systems can be obtained from analysis of the (II/I) potentials from Table 1. In order to access the Re(I) fragment, a reducing agent with a potential of around −2 V (NHE) would be required.

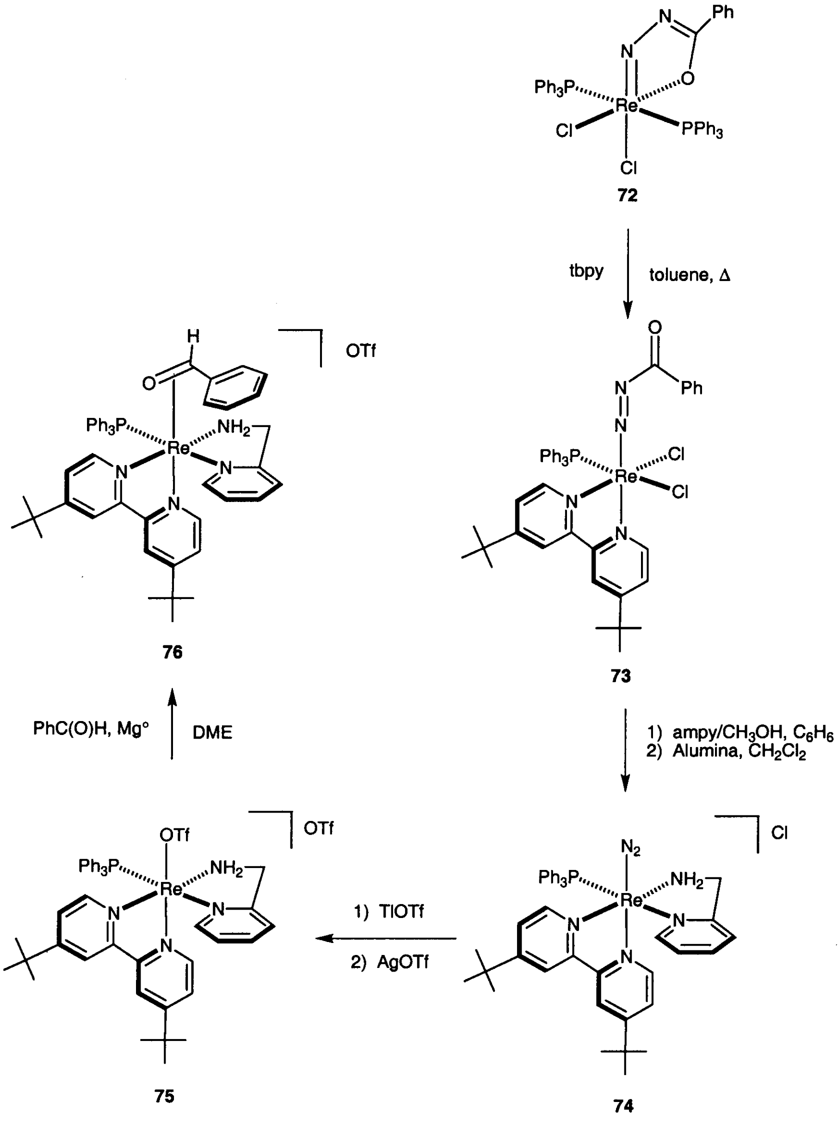
Accordingly, while the pentaaminerhenium(III/II) systems have been shown to be strong π-bases, attempted reductions with Na^0 or Mg^0 in the presence of aromatic ligands such as benzene or anisole have produced no trace of dihapto-coordinated aromatic complexes. The primary conclusion drawn from the development of the pentaaminerhenium(III/II) systems was that the electronics of the rhenium center had to be moderated in order to obtain Re(I) dearomatization agents. Thus, attention in our laboratory turned to pyridyl and other π-acceptor ligands to abate the electronic environment of the rhenium centers.

3.2.2. Rhenium-pyridyl systems

Chatt et al. have demonstrated that the chelate $Re({=}NN{=}C(Ph)O{-})(PPh_3)_2Cl_2$ is a useful precursor to several rhenium(I) dinitrogen species [95,96]. The reduction of the rhenium(V) chelate to the dinitrogen complex has been accomplished through a diazenido Re(III) intermediate of the form Re(–N=NC(O)Ph)(L)$_5$ (where L = phosphines and halides). Further addition of phosphines in MeOH yields the Re(I) dinitrogen species after displacement of the chlorides and reduction of the diazenido ligand. It was hoped that these Re(I) dinitrogen complexes could be oxidized back to Re(II) in the presence of a weakly coordinating counter ion (e.g. OTf$^-$) to give a Re(II) dearomatization precursor similar to the Os(III) system [Os(NH$_3$)$_5$(OTf)][OTf]$_2$.

Synthetic attempts in our laboratory have focused on analogous syntheses using amine and pyridyl ligands rather than phosphines. Accordingly, reduction of the chelate Re(=NN=C(Ph)O–)(PPh$_3$)$_2$Cl$_2$ (**72**) (Scheme 31) with 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbpy) in refluxing toluene yields the diazenido rhenium(III) complex Re(–N=NC(O)Ph)(tbpy)(PPh$_3$)Cl$_2$ (**73**) [97]. Subsequent addition of ampy in refluxing benzene and MeOH affords the Re(I) dinitrogen complex [Re(N$_2$)(tbpy)(ampy)(PPh$_3$)][OTf] (**74**). Counter ion metathesis with TlOTf followed by oxidation with AgOTf gives the Re(II) triflato complex [Re(OTf)(tbpy)(ampy)(PPh$_3$)][OTf] (**75**). Analogous complexes of the form [Re(N$_2$)(ampy)$_2$(PPh$_3$)][OTf] and [Re(N$_2$)(en)(ampy)(PPh$_3$)][OTf] have been synthesized in a similar manner. Reduction of the triflato complex [Re(OTf)(tbpy)(ampy)(PPh$_3$)][OTf] in the presence of a variety of ligands (ethylene, CO, ^{t}BuNC, and benzaldehyde) yields the corresponding Re(I) substitution products. The most significant complex synthesized in this manner is the benzaldehyde complex [Re(*C*,*O*-η^2-(benzaldehyde))(tbpy)(ampy)(PPh$_3$)][OTf] (**76**). This system is similar spectroscopically to aldehyde complexes produced by Gladysz et al. containing the {CpRe(NO)(PPh$_3$)}$^+$ fragment [98,99]. Unfortunately, attempts to coordinate aromatic ligands failed to produce any trace of the bound aromatic ligand. The II/I potential for **76** is about 0.5 V more negative than the analogous pentaammineosmium(II) system [100,101], but still in the correct range for coordinating aromatic molecules. Accordingly, the lack of success in producing dihapto-coordinated aromatic complexes with this fragment is most likely a result of the steric bulk of the rhenium fragment.

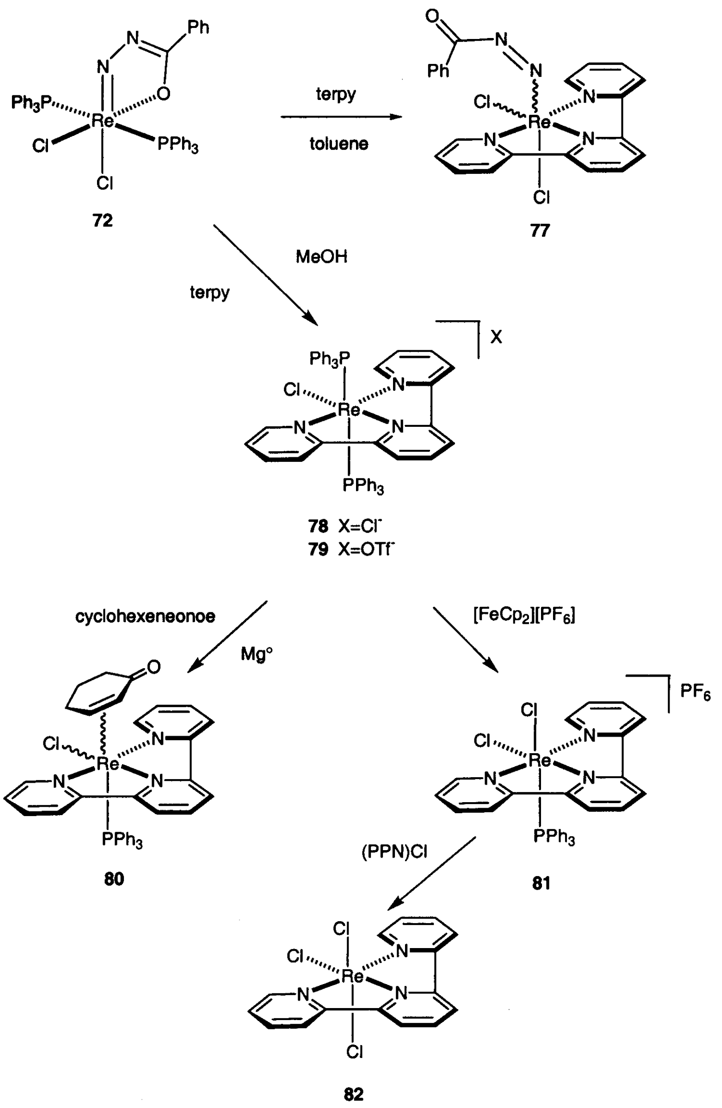
The chelate **72** has also provided a convenient route into terpyridyl chemistry. Complex **72** affords the diazenido complex [Re(terpy)(–N=NC(O)Ph)(Cl)$_2$] (**77**) (terpy = 2,2′,2″-terpyridyl) in toluene, while the analogous reaction in MeOH gives either the chloride or triflate salts of [Re(terpy)(PPh$_3$)$_2$(Cl)]$^+$ (**78** and **79**) (Scheme 32). The bis(phosphine) complexes **78** and **79** have proven to be useful precursors to several Re-terpyridyl species. Oxidation of **78** with [FeCp$_2$]$^+$ allows the removal of a triphenylphosphine ligand to form the bis(chloride) rhenium(III) complex [Re(terpy)(PPh$_3$)Cl$_2$][PF$_6$] (**81**). Addition of a soluble chloride source such as [PPN][Cl] {PPN = bis(triphenylphosphoranylidene)ammonium} results in the dissociation of the other phosphine ligand to produce the tris(chloride) complex Re(terpy)Cl$_3$ (**82**). Perhaps the most relevant rhenium–terpy system produced from the bis(triphenylphosphine) complex is the cyclohexenone rhenium(I) derivative Re(terpy)(PPh$_3$)Cl(*C*,*C*-η^2-cyclohexenone) (**80**). The cyclohexenone complex was produced by reduction of **79** with Mg^0 in the presence of the ligand. In contrast to



Scheme 31.

the $\{CpRe(NO)(PPh_3)\}^+$ system [102], there is no spectroscopic or electrochemical evidence for the η^1-ketone isomer.

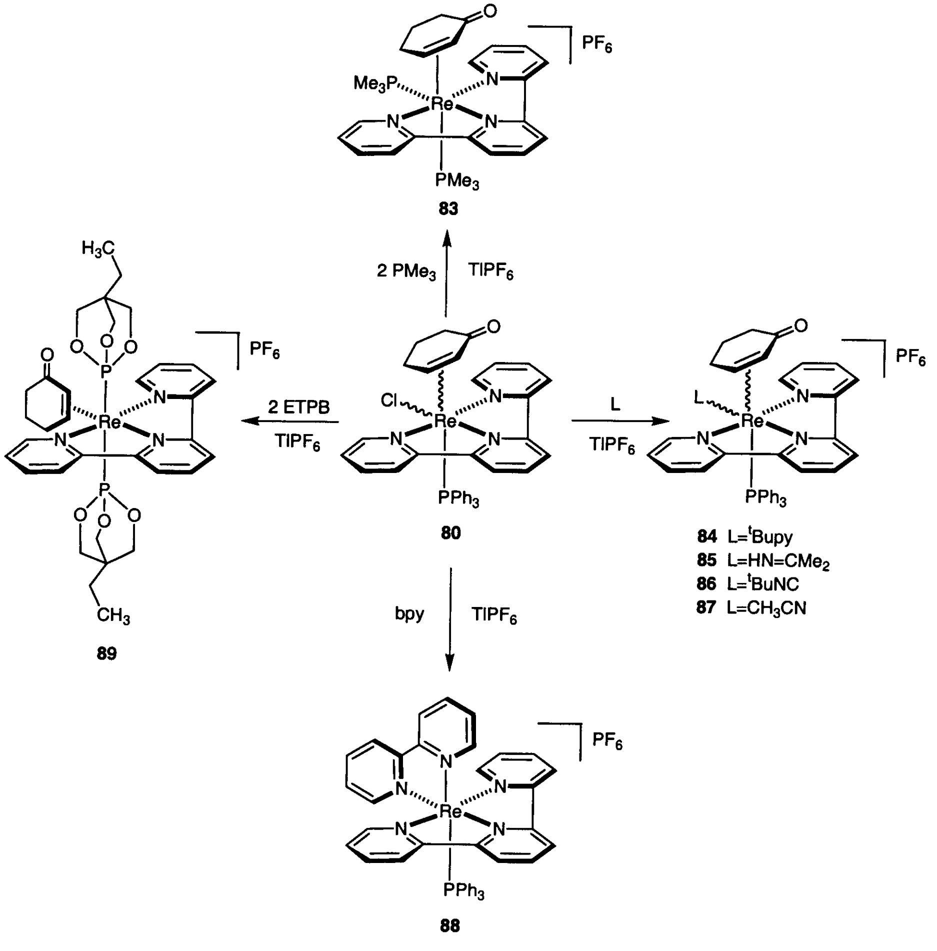
Substitution of the chloride ligand of $Re(terpy)(PPh_3)Cl(C,C\text{-}\eta^2\text{-cyclohexenone})$ (**80**) with several simple ligands affords the rhenium(I) analogs $[Re(terpy)(PPh_3)(L)][PF_6]$ {where L = 4-*tert*-butylpyridine (^{t}Bupy) (**84**), $HN{=}CMe_2$ (**85**), ^{t}BuNC (**86**), CH_3CN (**87**)} (Scheme 33). The imine complex **85** is formed from the condensation of NH_3 (the desired ligand) and acetone (the solvent). Addition of



Scheme 32.

an excess of sterically bulky ligands such as PMe_3 or 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB) to **80** affords the double substitution products $[Re(terpy)(PMe_3)_2(C,C\text{-}\eta^2\text{-cyclohexenone})][PF_6]$ (**83**), $[Re(terpy)(bpy)(PPh_3)][PF_6]$ (**88**) and $[Re(terpy)(ETPB)_2(C,C\text{-}\eta^2\text{-cyclohexenone})][PF_6]$ (**89**) following chloride extraction with thallium. Despite the fact that the terpy–bpy system $[Re(terpy)(bpy)(PPh_3)][PF_6]$ (**88**) contains no strong π-acid ligands, it has been found to be stable to refluxing conditions (in basic MeOH) as well as to substitution by the π-acidic ETPB ligand.

Use of even mild oxidants such as AgOTf has proven to be unsuccessful with the imine complex **85**, PMe_3 complex **83** and ^{t}Bupy complex **84** in attempts to synthesize Re(II) precursors for binding of aromatic ligands. For example, silver is not powerful enough to oxidize the ETPB or ^{t}BuNC complexes due to the relatively electron-deficient nature of these species. In contrast, the bpy complex $[Re(terpy)(bpy)(PPh_3)][PF_6]$ (**88**) has been successfully oxidized to its Re(II) analog upon treatment with AgOTf. Unfortunately, further oxidation occurs in acetone to yield the putative Re(III) binuclear system $[\{Re(terpy)(bpy)\}_2(\mu\text{-}O)]^{4+}$. Electrochemical data for several of the terpyridyl complexes listed above are summarized in Table 3. The most notable feature of the potentials catalogued is the variance in II/I reduction potentials observed by varying a single ligand. Many of the terpy–cyclohexenone complexes (**80**–**88**, **89**) have d^5/d^6 potentials in the expected range for



Scheme 33.

Table 3
Reduction potentials for Re(I), Re(II) and Re(III) terpyridyl complexes[a]

Compound (no.)	IV/III	III/II	II/I	I/0
[Re(terpy)$(PPh_3)_2$Cl]Cl (**78**)	1.16[b]	0.48[b]	−1.02	−1.89
[Re(terpy)$(PPh_3)_2$Cl]OTf (**79**)	1.18[b]	0.51	−0.99	−1.89
[Re(terpy)$(PPh_3)Cl_2$]PF_6 (**81**)	1.18[b]	0.06	−1.32[c]	–
Re(terpy)Cl_3 (**82**)	0.52	−0.49	−1.51[b]	–
[Re(terpy)(PPh_3)Cl(η^2-cyclohexenone)] (**80**)	–	0.94	0.04	−1.46[b]
[Re(terpy)$(PMe_3)_2$(η^2-cyclohexenone)]PF_6 (**83**)	–	1.26[b]	0.36	−1.36
[Re(terpy)(PPh_3)(^{t}Bupy)(η^2-cyclohexenone)]PF_6 (**84**)	–	–	0.50[b]	−1.24
[Re(terpy)(PPh_3)(NH=CMe_2)(η^2-cyclohexenone)]PF_6 (**85**)	–	1.10[b]	0.18	−1.34
[Re(terpy)(PPh_3)(^{t}BuNC)(η^2-cyclohexenone)]PF_6 (**86**)	–	1.24[b]	0.18	−1.34
[Re(terpy)$(PPh_3)(CH_3CN)$(η^2-cyclohexenone)]PF_6 (**87**)	–	1.30[b]	0.42	−1.22[c]
[Re(terpy)$(ETPB)_2$(η^2-cyclohexenone)]PF_6 (**89**)	–	–	0.66	−1.38[c]
[Re(terpy)(bpy)(PPh_3)]PF_6 (**88**)	–	1.00[b]	−0.14	−1.46[c]

[a] DMAc, 100 mV/s, TBAH electrolyte.

[b] Reported value is for $E_{p,a}$.

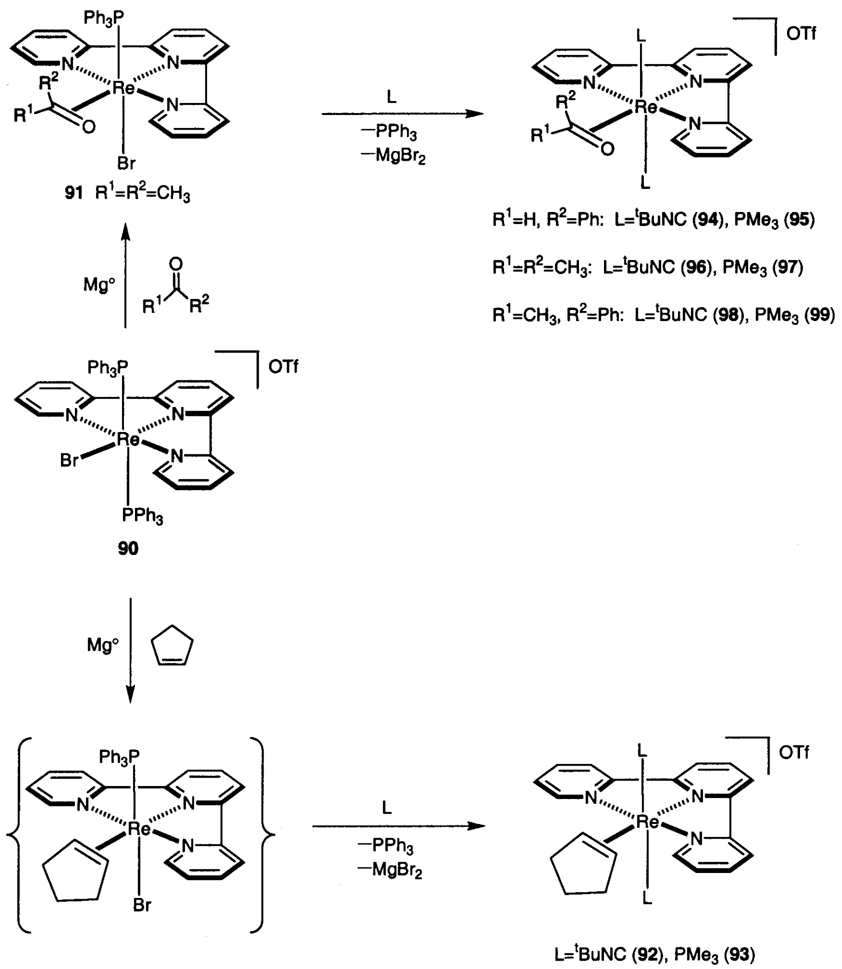
[c] Reported value is for $E_{p,c}$.

coordination of aromatic molecules but suffer from instability and large steric profiles.

Despite these problems, other attempts were made to utilize rhenium–terpy systems to bind unsaturated ligands by replacing the chloride ligand of the bis(triphenylphosphine) complexes **78** and **79** with a better leaving group. It has been found that the bromide analog, [Re(terpy)$(PPh_3)_2$Br][OTf] (**90**) (Scheme 34) could be synthesized from the bromide chelate Re(=NN=C(Ph)O–)$(PPh_3)_2Br_2$. Reduction of the bromide complex with Mg^0 yields the putative Re(I) complexes of the form [Re(L_π)(terpy)(Br)(PPh_3)] (where L_π = cyclopentene, benzaldehyde, acetone and acetophenone). While these species have been detected by cyclic voltammetry, only the acetone complex **91** has been isolated. The in situ addition of two equivalents of PMe_3 or ^{t}BuNC displaces the bromide and remaining triphenylphosphine to give isolable olefin, aldehyde and ketone complexes of the type [Re(L_π)(terpy)$(L)_2$][OTf] {where L = ^{t}BuNC (**92**, **94**, **96**, and **98**) or PMe_3 (**93**, **95**, **97**, and **99**)} [103].

The electrochemical data of complexes **92**–**99** are summarized in Table 4. The electron density of the metal center is moderated by the π-acidic ^{t}BuNC ligands relative to the σ-donating PMe_3 ligands. The olefin complexes exhibit reversible oxidation waves, while the coordinated aldehydes and ketones display irreversible oxidations. Presumably, the ability of the carbonyl-containing compounds to coordinate η^1 through the oxygen results in the irreversible characteristics of the II/I wave for these complexes. Similar behavior is observed with the pentaammineosmium(II) system [100,101,104,105].

Addition of methyl triflate to the acetone complex *trans*-[Re(η^2-acetone)(terpy)(^{t}BuNC)$_2$][OTf] (**96**) affords the *O*-methylated product *trans*-[Re{η^2-



Scheme 34.

(Me)$_2$COMe}(terpy)(^{t}BuNC)$_2$][OTf]$_2$ (**100**) (Scheme 35). Thus, even with the π-acidic isonitrile ligands, the rhenium fragment acts as a π-base to activate the ketone toward electrophilic addition similar to that seen with the $\{Os(NH_3)_5\}^{2+}$ fragment [106]. The ketonium ligand can be described by two different resonance structures (**I** and **II**). Structure **I** represents the η^2-ketonium form while structure **II** is formally a Re(III) methoxymethyl species. The most pertinent data which indicates that form **I** is a more accurate model for the actual system includes a downfield shift for the bound carbon atom resonance from 89.6 ppm in the parent acetone to 92.1 ppm for the ketonium product. This shift is in the opposite direction from that expected for structure **II**.

In order to develop more general transformations with these ligands, attention in our laboratory turned to a different route into polypyridyl Re(I) systems. The

Table 4
Cyclic voltammogram data for selected terpyridyl complexes

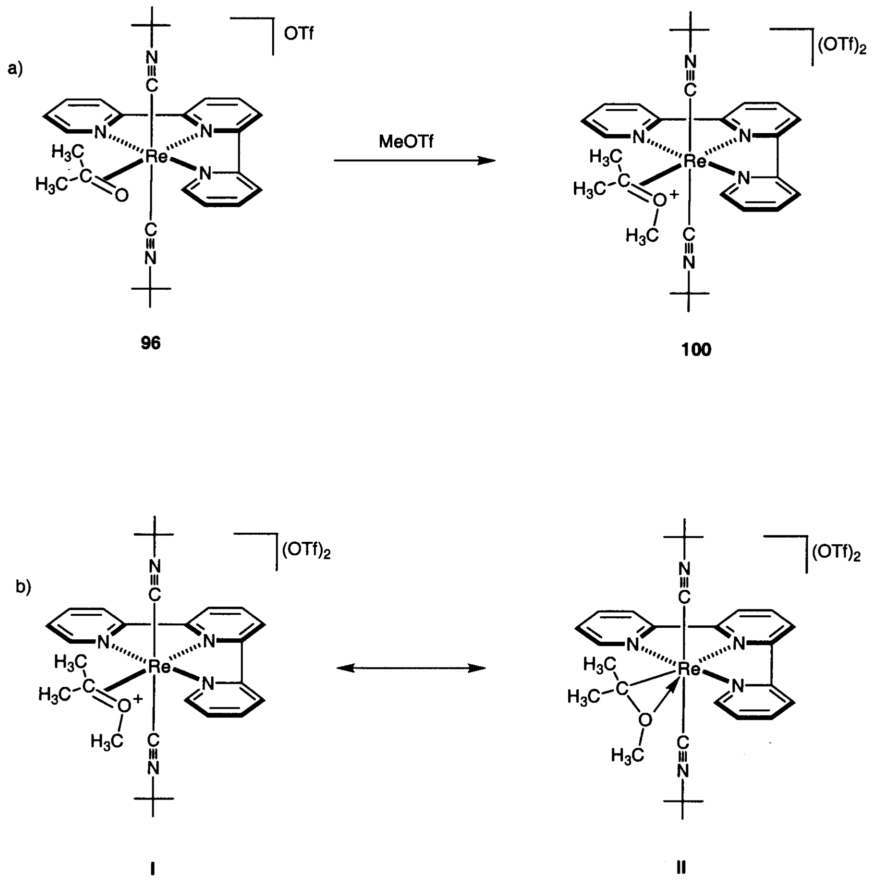
Complex (number)	Re(II/I)[a]	Re(I/0)[a]
$[\text{Re(terpy)}(^t\text{BuNC})_2(\eta^2\text{-cyclopentene})][\text{OTf}]$ (**92**)[b]	0.52	−1.38
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2\text{-cyclopentene})][\text{OTf}]$ (**93**)[b]	0.22	−1.42
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2\text{-benzaldehyde})][\text{OTf}]$ (**95**)[c]	0.28	−1.44
$\text{Re(terpy)Br)(PPh}_3)(\eta^2\text{-acetone})$ (**91**)[c]	−0.04[d]	−1.38
$[\text{Re(terpy)}(^t\text{BuNC})_2(\eta^2\text{-acetone})][\text{OTf}]$ (**96**)[b]	0.46[d]	−1.42
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2\text{-acetone})][\text{OTf}]$ (**95**)[c]	0.08[d]	−1.46
$[\text{Re(terpy)}(^t\text{BuNC})_2(\eta^2\text{-acetophenone})][\text{OTf}]$ (**98**)[c]	0.34	−1.32
$[\text{Re(terpy)}(\text{PMe}_3)_2(\eta^2\text{-acetophenone})][\text{OTf}]$ (**99**)[c]	0.22[d]	−1.42

[a] Volts vs. NHE.

[b] In DMAc.

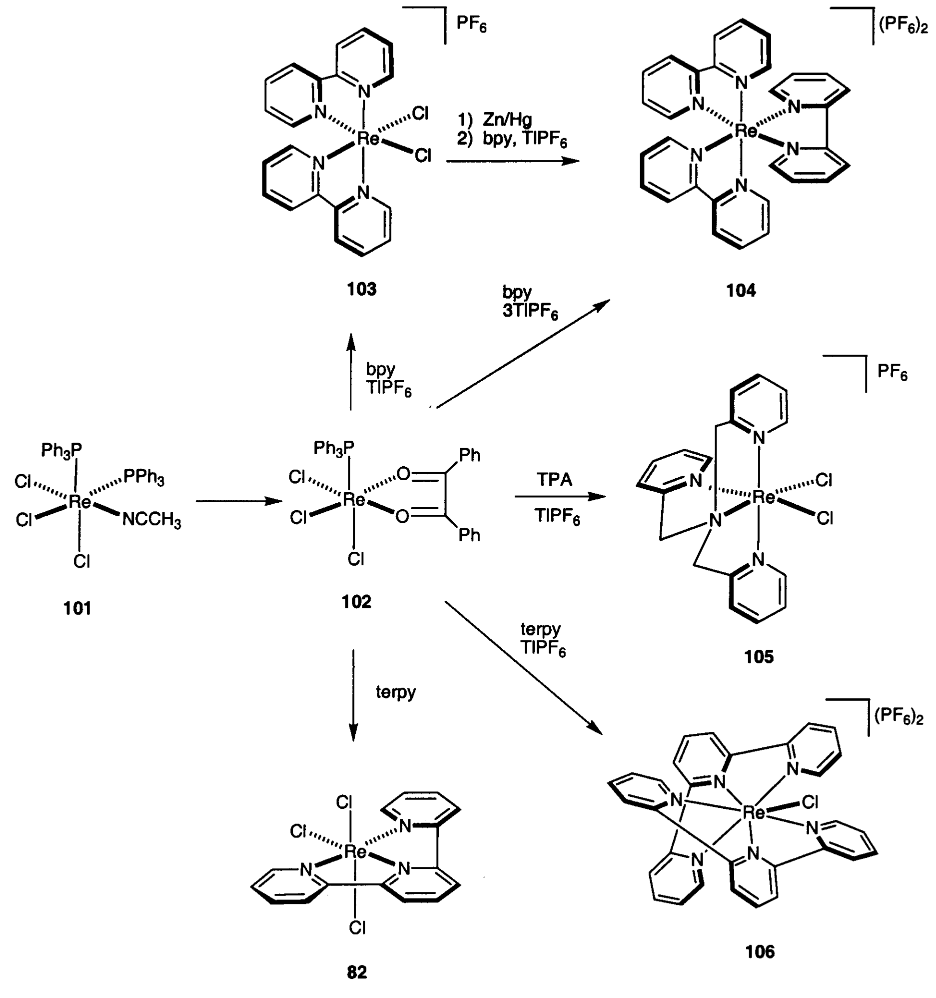
[c] In acetone.

[d] Reported for $E_{\text{p,a}}$.



Scheme 35.

Re(III) acetonitrile complex $Re(CH_3CN)(PPh_3)_2Cl_3$ (**101**) (Scheme 36) has been synthesized by Rouschias and Wilkinson [107] from $Re(O)Cl_3(PPh_3)_2$, CH_3CN and PPh_3 in toluene. Displacement of a chloride and PPh_3 ligand by benzil ($Ph(CO)_2Ph$) yields the versatile Re(III) precursor $Re(benzil)(PPh_3)Cl_3$ (**102**). From the benzil complex, polypyridyl complexes have been synthesized by utilizing the halide scavenger Tl^+ to selectively remove one, two or all three chloride atoms from the starting material to give complexes of the type *cis*-$[Re(L)_2Cl_2]^+$, $[Re(L)_3]^{2+}$, $Re(L')Cl_3$, $[Re(L')_2Cl]^{2+}$, and $[Re(L'')Cl_2]^+$ {where L = bpy (**103** and **104**), tbpy, 1,10-phenanthroline (phen), L′ = terpy, (**82** and **106**) and L″ = TPA (tris(2-pyridylmethyl)amine) (**105**)} [108]. Thallium is not necessary to form the terpy–tris(chloride) complex **82** which has also been synthesized from the bis(triphenylphosphine) complex $[Re(terpy)(PPh_3)_2Cl][Cl]$ (**78**) (see Scheme 32).



Scheme 36.

Again, electrochemistry provides a gauge of the electronic environment of the metal center for these complexes. Table 5 lists the reduction potentials for several of the polypyridyl complexes described above. The electronic progression observed for the $[Re(en)_2Cl_2]^+$ and $[Re(ampy)_2Cl_2]^+$ systems, with III/I and III/II potentials at -1.88 and -1.15 V, respectively (vide supra), reflects the attenuation of the electron density upon introduction of the pyridyl ligands. Similarly, the d^4/d^5 potential for $[Re(TPA)Cl_2][PF_6]$ (**105**) is shifted to -0.91 V, which is consistent with replacing one of the donating amine groups of the bis(ampy) fragment with a more withdrawing pyridyl ligand. What appears to be an inordinate positive shift in the III/II potential to -0.21 V has been observed for the complex $[Re(bpy)_2Cl_2][PF_6]$ (**103**). The large positive shift in the reduction potential for **103** is a result of the enhanced π-acidity of the conjugated pyridyl ligands. Another indication of the increased π-acidic nature of the conjugated pyridyl ligands is obtained by comparison of the terpy and pyridine tris(chloride) complexes. The III/II potential for $Re(terpy)Cl_3$ (**82**) is shifted over 0.6 V more positive than the analogous complex *mer*-$Re(py)_3Cl_3$ [108]. Thus, a wide range of electronic environments are accessible with the rhenium–pyridyl systems. Unfortunately, steric issues and the inability to produce clean reduction conditions render these systems impractical for dearomatization methodologies.

Table 5
Summary of the reduction potentials for polypyridyl complexes

Complex (number)	IV/III	III/II	II/I	I/0	0/−I
cis-$[Re(bpy)_2Cl_2]^+$ (**103**)	0.99^a	-0.20	-1.01		
cis-$[Re(tbpy)_2Cl_2]^+$	0.96^a	-0.30	-1.14		
cis-$[Re(phen)_2Cl_2]^+$	0.95^a	-0.25	-0.94		
$ReCl_3(terpy)$ (**82**)	0.52	-0.49	-1.51^b		
$[Re(TPA)Cl_2]^+$ (**105**)	0.81^a	-0.91	-1.85^b		
cis-$[Re(bpy)_2(OMe)_2]^+$	0.53^a	-0.81	-1.34		
$[Re(terpy)_2Cl]^{2+}$ (**106**)	1.37	-0.53^b			
$[Re(bpy)_2Cl_2(^tBuNC)]^+$	1.12	-0.85^b			
$[Re(tbpy)_2Cl_2(^tBuNC)]^+$	1.05	-1.06^b			
$[Re(phen)_2Cl_2(^tBuNC)]^+$	1.10	-0.61^b			
$[Re(bpy)_2(^tBuNC)_3]^{3+}$		-0.61^b			
$[Re(bpy)_3(^tBuNC)]^{3+}$		-0.39^b			
$[Re(bpy)_3]^{2+}$ (**104**)		$+0.50^b$	-0.33	-1.22	-1.62
$[Re(tbpy)_3]^{2+}$		$+0.49^b$	-0.47	-1.35	-1.75
$[Re(phen)_3]^{2+}$		$+0.56^a$	-0.31	-1.21	-1.58
cis-$[Re(bpy)_2(^tBuNC)_2]^+$		1.18^a	0.22	-1.30	-1.62
$[Re(terpy)_2]^+$		0.36^a	0.12	-1.42	-1.76

[a] Reported values are for $E_{p,a}$.

[b] Reported values are for $E_{p,c}$.

3.3. Rhenium dinitrogen complexes and the introduction of a single strong π-acid into the ligand set

Based on the knowledge gained from the development of the pentaaminerhenium and pyridyl systems, we have been able to narrow the electronic and steric characteristics needed to coordinate aromatic ligands. The polypyridyl systems in particular have demonstrated that electron-rich rhenium systems can be developed with primarily σ-donor ligands, and that these systems can be used to coordinate a variety of unsaturated ligands such as olefins, aldehydes and ketones. The π-basicity of these rhenium species has also been demonstrated by the ability of the terpyridyl systems to activate ketones toward electrophilic addition. Perhaps most importantly, cyclic voltammetry indicates that a wide range of electronic characteristics are available depending on the ancillary ligands employed. The steric profile of the pentaaminerhenium complexes seems ideal for coordination of aromatic ligands, but these systems are too electron-rich for reduction to Re(I). In contrast, the polypyridyl systems are, in many cases, electronically very close to the pentaammineosmium(II) system, but suffer from sterically congested coordination sites. Thus, we attempted to develop a synthetic strategy in which the ligand set of the rhenium species was systematically altered in order to arrive at the proper balance between electronic and steric characteristics needed to coordinate aromatic ligands.

3.3.1. Rhenium(II/I) dinitrogen complexes

The synthesis of dinitrogen complexes of rhenium(I) has proven to be desirable in several ways. Firstly, the use of dinitrogen species directly parallels the synthetic procedure used for the $\{Os(NH_3)_5\}^{2+}$ fragment. Oxidation of $[Os(NH_3)_5(N_2)][OTf]_2$ with HOTf and Br_2 yields the Os(III) precursor $[Os(NH_3)_5(OTf)][OTf]_2$ [15,87,88]. It was hoped that a rhenium(I) dinitrogen analog would be susceptible to the same oxidation chemistry in the presence of a triflate source to give analogous Re(II) precursors. In addition, Re(I) dinitrogen complexes offer the advantage of a convenient IR stretching frequency for the bound N_2 ligand, which can be correlated with electrochemical data to provide a picture of the electronic characteristics of the metal center. Thus, we sought a general route to dinitrogen complexes, which could be tuned electronically to afford a rhenium(I) center that matched the electronic properties of the pentaammineosmium(II) system. In addition, the synthetic methodology should ideally produce a chiral dinitrogen complex, which could be resolved to give the appropriate asymmetric Re(II) precursor for coordination of aromatic molecules. Accordingly, the method used earlier for the production of the dinitrogen species $[Re(N_2)(tbpy)(PPh_3)(ampy)]Cl$ (**74**) (see Scheme 31) was revisited, and alteration of the steric and electronic characteristics of the rhenium(I) center was undertaken.

A variety of dinitrogen complexes[109] have been synthesized from the chelate $Re(=NN=C(Ph)O-)(PPh_3)_2Cl_2$ (**72**). In general, either an amine, pyridyl, phosphite, or π-acid ligand can be added to give a variety of diazenido species. Subsequent addition of another amine or pyridyl ligand affords dinitrogen complexes. In addition, several dinitrogen species have been produced directly from the chelate

Table 6
Infrared Spectroscopic and electrochemical data for rhenium(I/II) amine complexes

Compound (number)	ν_{NN} (KBr, cm^{-1})	$E_{1/2}$ (Re^I/Re^{II}; V, NHE)[a]
Rhenium(I)		
$[Re(N_2)(en)_2(PPh_3)][OTf]$	1872	−0.50
$[Re(N_2)(ampy)_2(PPh_3)][OTf]$	1915	−0.20
$[Re(N_2)(TPA)(PPh_3)][OTf]$	1920	0.18
$[Re(N_2)(tbpy)(PPh_3)(ampy)]Cl$	1940	−0.02
$[Re(N_2)(dien)(PPh_3)(ETPB)][OTf]$ isomer A	1986	0.26
$[Re(N_2)(dien)(PPh_3)(ETPB)][OTf]$ isomer B	1969	0.27
$[Re(N_2)(en)(PPh_3)_2(ETPB)][OTf]$	2004	0.78
$[Re(N_2)(bpy)(PPh_3)_2(ETPB)][OTf]$	2008	0.84
$[Re(N_2)(dien)(PPh_3)(PF_3)][OTf]$ (**107**)	2033	0.86
$[Re(N_2)(dien)(PPh_3)(CO)][OTf]$ (**123**)	2036	0.74
Rhenium(II)		
$[Re(N_2)(TPA)(PPh_3)][OTf]_2$	2054	0.18
$[Re(N_2)(ampy)_2(PPh_3)][OTf]_2$	2030	−0.20
$[Re(N_2)(en)_2(PPh_3)][OTf]_2$	1998	−0.50

[a] Reversible couples recorded in DMAc solution.

72. Table 6 summarizes the electrochemical and infrared spectroscopic data for several of the dinitrogen complexes produced in this manner. The electronics of these systems are so diverse, that several of the more electron-rich dinitrogen systems have been proven to be stable at the Re(II) state. Significantly, the compounds closest electronically to the pentaammineosmium(II) system are the PF_3 and CO systems *fac*-$[Re(N_2)(dien)(PPh_3)(PF_3)][OTf]$ (**107**) and *fac*-$[Re(N_2)(dien)(PPh_3)(CO)][OTf]$ (**123**) (dien = diethylenetriamine). This can be more

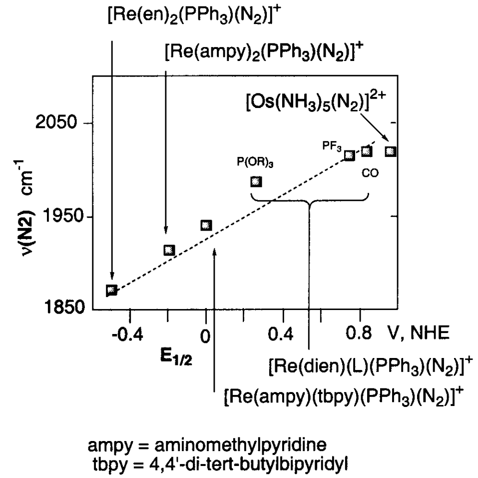


Fig. 1.

clearly seen when the data in Table 6 is graphed (Fig. 1). Thus, the use of the PF_3 and CO systems to coordinate unsaturated ligands was pursued.

3.3.2. The asymmetric π-bases fac-{Re(dien)(PPh₃)(PF₃)}⁺ and fac-{Re(dien)(PPh₃)(CO)}⁺

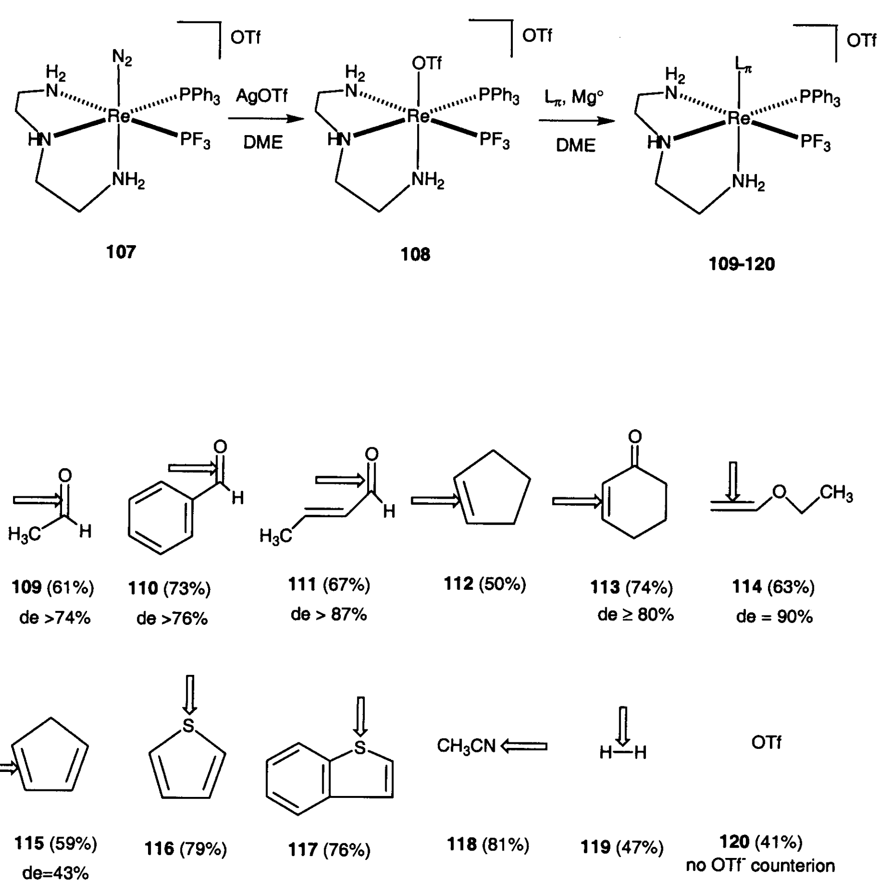
While the introduction of strong π-acids into the ligand set of potential dearomatization agents seems counterintuitive to our intended purpose, the data presented in Fig. 1 illustrates the importance of these ligands in moderating the electronic characteristics of the rhenium(I) centers. Our initial choice of the less prevalent PF_3 ligand may also seem unnecessarily exotic. The logic for employing PF_3 versus CO simply involved the relative lack of reactivity of the former once coordinated to the metal. Thus, while CO is known to bridge metals and undergo attack itself, the trifluorophosphine ligand is more inert. Once the range of unsaturated ligands which were coordinated by the PF_3 system was exhausted, the carbonyl analog was prepared for comparison (vide infra).

Oxidation of the PF_3 dinitrogen complex *fac*-[Re(N_2)(dien)(PPh_3)(PF_3)][OTf] (**107**) with AgOTf in 1,2-dimethoxyethane (DME) gives the convenient Re(II) triflato precursor *fac*-[Re(OTf)(dien)(PPh_3)(PF_3)][OTf] (**108**) (Scheme 37) in moderate yield (39%) [109]. Subsequent reduction of this complex in DME with Mg^0 and an unsaturated ligand L_π affords a variety of rhenium(I) complexes of the form *fac*-[Re(L_π)(dien)(PPh_3)(PF_3)][OTf] {where L_π = aldehydes (**109**–**111**), olefins (**112**), enones (**113**), vinyl ethers (**114**), dienes (**115**) and nitriles (**118**)} [110]. Of all the rhenium π-bases catalogued thus far, the *fac*-{Re(dien)(PPh_3)(PF_3)}$^+$ fragment shows the greatest propensity to coordinate a variety of unsaturated ligands.

The only aromatic ligands which have been shown to coordinate the *fac*-{Re(dien)(PPh_3)(PF_3)}$^+$ fragment are thiophene and benzothiophene (**116** and **117**). Unfortunately, both ligands are bound through their sulfur atoms. The dihydrogen complex *fac*-[Re(H_2)(dien)(PPh_3)(PF_3)][OTf] (**119**) has also been synthesized by reduction of the **105** under a purge of hydrogen gas. Complex **119** exhibits an elongated H–H bond length of 1.38 ± 0.03 Å (estimated from HD coupling) [109]. The product obtained after reduction of **108** with no ligand present contains electrochemical and spectroscopic data consistent with the rearranged triflato complex *mer*-[Re(OTf)(dien)(PPh_3)(PF_3)] (**120**).

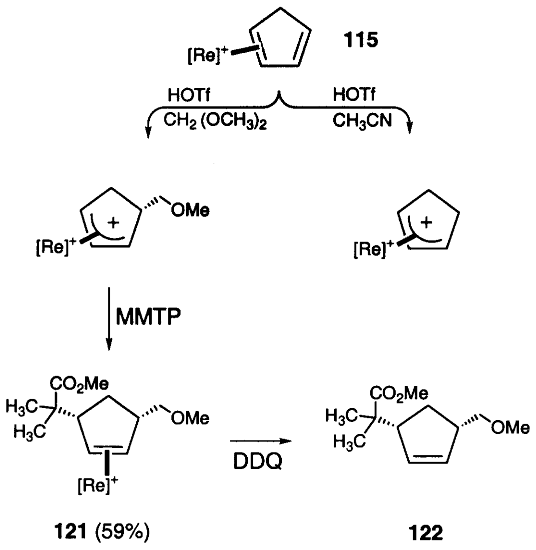
Also worth noting is the observation that the cyclopentadiene complex *fac*-[Re(η^2-cyclopentadiene)(dien)(PPh_3)(PF_3)][OTf] (**115**) is amenable to sequential electrophilic/nucleophilic additions with dimethoxymethane and 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP) to give the disubstituted cyclopentene complex *fac*-[Re{η^2-3-(2-carbomethoxy-2-propyl)-5-(methoxymethyl)cyclopentene}-(dien)(PPh_3)(PF_3)][OTf] (**121**) (Scheme 38) in good yield. Oxidation of **121** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) affords the free organic **122** exclusively as the *cis* isomer [110,111].

As previously mentioned, the carbonyl analog of the PF_3 dinitrogen complex has been prepared for comparative purposes. The PF_3 and CO ligands possess similar π-acidic character as evidenced by the relative II/I potentials and ν_{NN} values for the analogous dinitrogen complexes **107** and **123** (vide supra). However, when the



Scheme 37.

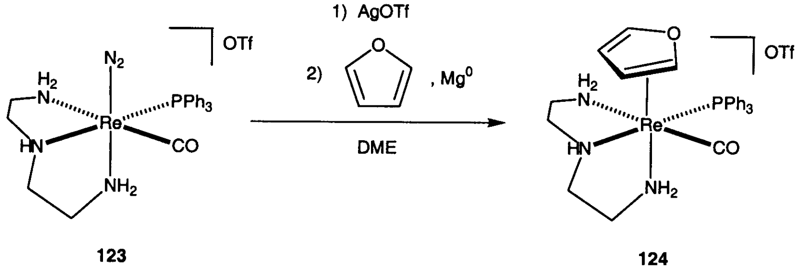
carbonyl complex *fac*-[Re(N_2)(dien)(PPh$_3$)(CO)][OTf] is exposed to an oxidation/reduction sequence with AgOTf and Mg^0 in the presence of furan, the dihapto coordinated furan complex *fac*-[Re(η^2-furan)(dien)(PPh$_3$)(CO)][OTf] (**124**) (Scheme 39) is isolated in good yield (86%). The most convincing evidence for dihapto coordination of furan has been obtained from the ^{13}C-NMR data. The ^{13}C furan resonances for **124** appear at 143, 110, 93 and 47 ppm. All of these values are within 4 ppm of the analogous pentaammineosmium(II) complex [26]. Also of note is the half-life of *fac*-[Re(η^2-furan)(dien)(PPh$_3$)(CO)][OTf] in acetone-d_6, which has been found to be approximately 1 day. The cyclic voltammogram of **124** includes a broad irreversible oxidation wave at 0.61 V, which is also consistent with the potential observed for [Os(η^2-furan)(NH$_3$)$_5$][OTf]$_2$. The similarities between the electronic characteristics of the *fac*-{Re(dien)(PPh$_3$)(PF$_3$)}$^+$ and *fac*-{Re(dien)(PPh$_3$)(CO)}$^+$ fragments and the pentaammineosmium(II) system are illustrated in Table 7. Perhaps the most impressive characteristic of *fac*-[Re(η^2-furan)(dien)(PPh$_3$)(CO)][OTf] in relation to the complexes of *fac*-



Scheme 38.

$\{Re(dien)(PPh_3)(PF_3)\}^+$ is the fact that only a single diastereomer is observed for complex **124**.

Thus, *fac*-[Re(η^2-furan)(dien)(PPh$_3$)(CO)][OTf] represents the first example of a thermally stable η^2-coordinated complex of furan other than the pentaammineosmium(II) system. Unfortunately, the utility of the *fac*-$\{Re(dien)(PPh_3)(CO)\}^+$ fragment as a dearomatization agent is limited since no clean addition reactions have been observed for complex **124** and since furan is the only aromatic ligand shown to coordinate to this rhenium(I) center. At this stage, the electronic characteristics of the rhenium center had been tuned to a point where an aromatic ligand was coordinated in a dihapto fashion to rhenium. The primary weakness of the *fac*-$\{Re(dien)(PPh_3)(PF_3)\}^+$ and *fac*-$\{Re(dien)(PPh_3)(CO)\}^+$ fragments is the steric profile around the coordination site. All of the dinitrogen complexes listed in Table 6 suffer from the sterically demanding PPh$_3$ ligand being in a cis orientation



Scheme 39.

Table 7
Electrochemical data for $[Re(dien)(PPh_3)(PF_3)]^+$ and $[Re(dien)(PPh_3)(CO)]^+$ fragments

Compound (number)	$E_{1/2}$ (Re^I/Re^{II}; V, NHE)[a]
$[Re(OTf)(dien)(PPh_3)(PF_3)][OTf]$ (**108**)	−0.12
$[Re(\eta^2$-acetaldehyde$)(dien)(PPh_3)(PF_3)][OTf]$ (**109**)	0.88[b]
$[Re(\eta^2$-benzaldehyde$)(dien)(PPh_3)(PF_3)][OTf]$ (**110**)	0.62[b]
$[Re(\eta^2$-crotonaldehyde$)(dien)(PPh_3)(PF_3)][Otf]$ (**111**)	0.84[b]
$[Re(\eta^2$-cyclopentene$)(dien)(PPh_3)(PF_3)][OTf]$ (**112**)	0.54
$[Re(\eta^2$-cyclohexeneone$)(dien)(PPh_3)(PF_3)][OTf]$ (**113**)	1.07[b]
$[Re(\eta^2$-ethyl vinyl ether$)(dien)(PPh_3)(PF_3)][Otf]$ (**114**)	0.62[b]
$[Re(\eta^2$-cyclopentadiene$)(dien)(PPh_3)(PF_3)][OTf]$ (**115**)	0.51
$[Re(\eta^1$-thiophene$)(dien)(PPh_3)(PF_3)][OTf]$ (**116**)	0.28
$[Re(\eta^1$-benzo[*b*]thiophene$)(dien)(PPh_3)(PF_3)][OTf]$ (**117**)	0.29
$[Re(\eta^1$-acetonitrile$)(dien)(PPh_3)(PF_3)][OTf]$ (**118**)	0.11[c]
$[Re(H_2)(dien)(PPh_3)(PF_3)][OTf]$ (**119**)	1.15[b,c]
$[Re(OTf)(dien)(PPh_3)(PF_3)]$ (**120**)	−0.23
$[Re(\eta^2$-furan$)(dien)(PPh_3)(CO)][OTf]$ (**124**)	0.61[b]

[a] Recorded in DMAc at 100 mV s^{-1}.

[b] Reported values are for E_{pa}.

[c] Recorded in CH_3CN.

relative to the potential site of coordination. Even the relatively small steric difference between PF_3 and CO has proven to be vital in the coordination of furan by the *fac*-$\{Re(dien)(PPh_3)(CO)\}^+$ fragment. Armed with this knowledge and the observation that the carbonyl ligand was compatible with our methodology of developing dearomatization agents from high-valent rhenium, we turned our attention to alternative synthetic methodologies utilizing the hydridotris(pyrazolyl)-borate (Tp) ligand.

3.4. Synthesis and reactivity of hydridotris(pyrazolyl)borate complexes of rhenium

3.4.1. Introduction

In contrast to the CpRe systems which coordinate aromatic molecules in a dihapto fashion only at low temperatures (vide supra), the goal of our rhenium program has been to develop electron-rich systems which will form thermally stable η^2-coordinated complexes with aromatic molecules. In addition, Cp-containing complexes are known to undergo C–H activation with aromatic molecules [112–114]. Thus, in choosing a useful ligand set for dearomatization methodology, we avoided Cp ligands because of their ability to undergo electrophilic attack themselves and their propensity to facilitate formation of stable C–H activation products at the metal center (vide supra).

By comparison, the Tp ligand is also a monoanionic six-electron donor moiety which ligates to the metal in a facial fashion [115–117]. Furthermore, the strong σ-donating ability of the Tp class of ligands has been noted and this ligand is generally believed to be a poor π-acid [118]. Most importantly, in relation to the tendency of Cp systems to undergo oxidative addition, is the fact that Tp ligands have been purported to enforce the octahedral geometry of metal complexes [37,119–121]. Accordingly, a TpRe(L)(L′)(η^2-aromatic) fragment undergoing aromatic C–H oxidative addition would either proceed through a seven-coordinate intermediate (or transition state) or require cleavage of a rhenium ligand bond. Either of these pathways is likely to be of high energy and thus kinetically suppressed.

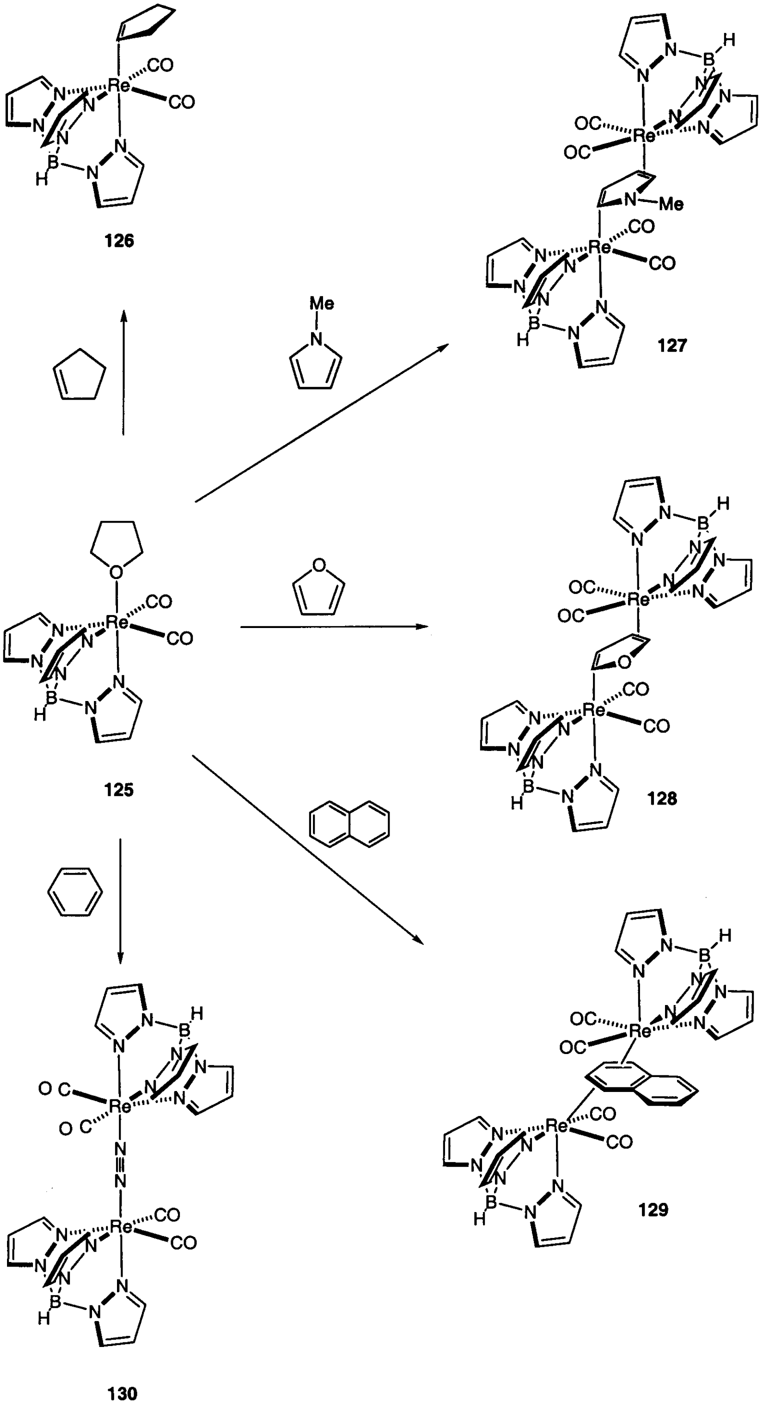
3.4.2. Reactions of TpRe(CO)$_2$(THF)

The TpRe(CO)$_2$(THF) complex has been reported to undergo ligand exchange reactions with acetonitrile, phosphines, pyridine and cyclohexylisonitrile [122]. This complex served as a gateway into TpRe chemistry for our group [123]. Although the presence of two strongly π-acidic ligands (two carbonyls) in the coordination sphere is counterintuitive to our intention of synthesizing electron-rich complexes, the facile access to a TpRe(I) fragment prompted initial study of this system.

Treatment of the complex TpRe(CO)$_2$(THF) (**125**) with excess cyclopentene yields the corresponding η^2-olefin complex **126** in good yield (66%) (Scheme 40). Spectroscopic data (^{1}H-NMR) are consistent with a fluxional process in which rapid rotation of the olefin is occurring. This observation is expected to be the case with two energetically similar and orthogonal dπ-orbitals. Reaction of the THF complex **125** with aromatic compounds yields dihapto-bound aromatic complexes. However, mononuclear η^2-aromatic complexes have proven to be thermally unstable and only binuclear complexes could be isolated {*N*-methylpyrrole complex (**127**) 35%; furan complex (**128**) 58%, naphthalene complex (**129**) 44%}. For example, the reaction of TpRe(CO)$_2$(THF) with excess furan yields {TpRe(CO)$_2$}$_2$(μ-2,3-η^2-4,5-η^2-furan) (**128**). Performing this reaction in neat furan suppresses the formation of binuclear complexes and allows spectroscopic observation of TpRe(CO)$_2$(η^2-furan).

Reaction of TpRe(CO)$_2$(THF) (**125**) with excess thiophene results in the displacement of the cyclic ether ligand with the sulfur heterocycle in 79% yield. Both NMR and electrochemical data indicate that the thiophene is sulfur-bound in a monohapto coordination mode. The thermodynamic preference for the sulfur bound isomer over the η^2-bound isomer is in accord with the observation that the mononuclear {TpRe(CO)$_2$(η^2-aromatic)} complexes are substitution labile. Thus, the two π-acidic carbonyl ligands render the metal center too electron-deficient to observe dihapto-binding of the thiophene ligand.

Interestingly, the {TpRe(CO)$_2$} fragment showed no propensity to bind benzene. Stirring a benzene solution of TpRe(CO)$_2$(THF) yields the dinitrogen-bridged complex {TpRe(CO)$_2$}$_2$(μ-N$_2$) (**130**) by coordination of nitrogen from the inert atmosphere. A similar reaction under an argon purge resulted in the observation of only starting material. This result is surprising since the {Cp*Re(CO)$_2$} fragment binds benzene (vide supra) [73]. Of note, the {TpRe(CO)$_2$} fragment appears to be slightly more electron-rich than the corresponding cyclopentadienyl fragment. For example, TpRe(CO)$_2$(THF) displays CO stretching frequencies at $\nu_{CO} = 1907$ and 1823 cm^{-1} while CpRe(CO)$_2$(THF) displays $\nu_{CO} = 1910$ and 1836 cm^{-1} (both



Scheme 40.

spectra were taken in THF) [122,124]. The ability of $\{Cp^*Re(CO)_2\}$ to bind benzene is likely a reflection of both the increased electron density due to the five methyl groups as well as a more sterically flexible metal coordination sphere compared to the Tp metal system.

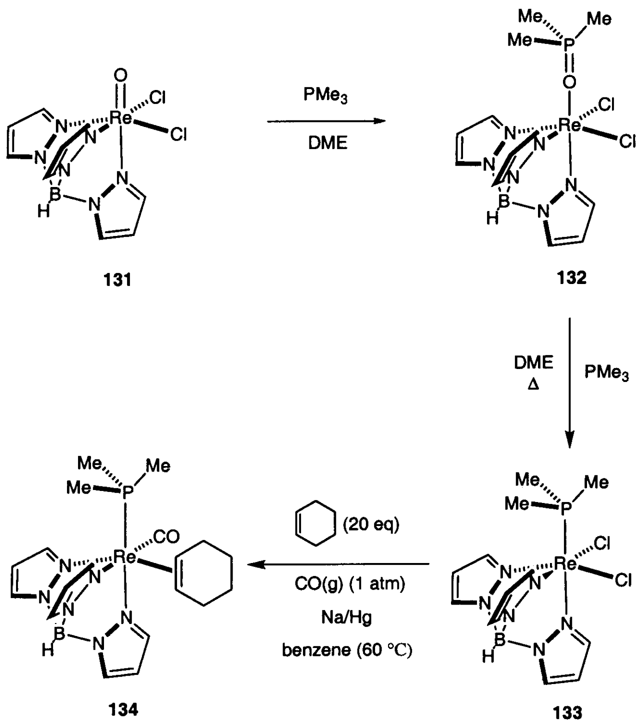
Although the formation of mononuclear dihapto-coordinated aromatic complexes was not realized with the $\{TpRe(CO)_2\}$ system, the ability of the Re(I) fragment to bind aromatics in a dihapto coordination mode is noteworthy. Especially important is the affinity to bind the *N*-methylpyrrole compound. To our knowledge, other than $[Os(NH_3)_5(\eta^2\text{-pyrrole})]^{2+}$ complexes (vide supra), the binuclear complex **127** bridged by *N*-methylpyrrole is the only example of an η^2-pyrrole complex. Accordingly, we reasoned that replacing one of the carbonyl ligands of the $\{TpRe(CO)_2\}$ fragment with a more donating moiety would result in a strongly π-basic fragment capable of forming thermally stable monomeric η^2-aromatic complexes.

3.4.3. Development of {TpRe(CO)(L)} fragments [125]

Starting with high valent Re(VII) was selected as the route to {TpRe(CO)(L)} systems. The synthesis of $TpRe(X)_2(O)\{X = Cl$ (**131**) or Br} complexes starting with $NaReO_4$ has been reported previously [126,127]. The oxo ligand of **131** is susceptible to nucleophilic attack, and reaction with PMe_3 yields the two-electron reduction product $TpRe(X)_2(O{=}PMe_3)$ (**132**) (Scheme 41). In refluxing DME the phosphineoxide ligand is labile [128], and a variety of Re(III) complexes of the type $TpRe(X)_2(L)$ can be accessed including the PMe_3 system **133**. The importance of the ability to systematically vary the steric and/or electron properties of L will be discussed below.

Reduction of $TpRe(Cl)_2(PMe_3)$ (**133**) in the presence of excess cyclohexene and CO(g) (1 atm) at approximately 60°C yields the rhenium(I) olefin complex $TpRe(CO)(PMe)_3(\eta^2\text{-cyclohexene})$ (**134**) in 61% yield after chromatographic workup. The low energy of the CO absorption (1796 cm^{-1}) and the II/I oxidation potential (0.23 V vs. NHE) of **134** are indicative of an electron-rich metal center. Corresponding III/II oxidation potentials for olefin complexes of pentaammineosmium(II) fall in the range of 0.5–0.6 V (NHE) [14]. Complex **134** is similar to a series of η^2-olefin complexes of the type $[Cp^xRe(PPh_3)(NO)(\eta^2\text{-olefin})]^+$ (Cp^x = cyclopentadienyl or pentamethylcyclopentadienyl) reported by Gladysz et al. [129–132].

At the rhenium(I) oxidation state, complex **134** is extremely stable. Even prolonged heating (several days) at temperatures of 60–70°C results in no signs of decomposition. Of note is the fact that no oxidative addition of the olefin to the electron-rich metal center is observed at these elevated temperatures. However, if the metal center is oxidized to Re(II), substitution for the olefin becomes accessible at reasonable temperatures. For example, treatment of **134** with a one-electron oxidant yields a new complex ($\nu_{CO} = 1912$ cm^{-1}) (Scheme 42), and this complex has been assigned as $[TpRe(CO)(PMe_3)(\eta^2\text{-cyclohexene})][OTf]$ (**135**). Brief reflux (approximately 15–30 minutes) of **135** in DME provides the triflate substituted product $TpRe(CO)(PMe_3)(OTf)$ (**136**) in quantitative yield by IR spectroscopy

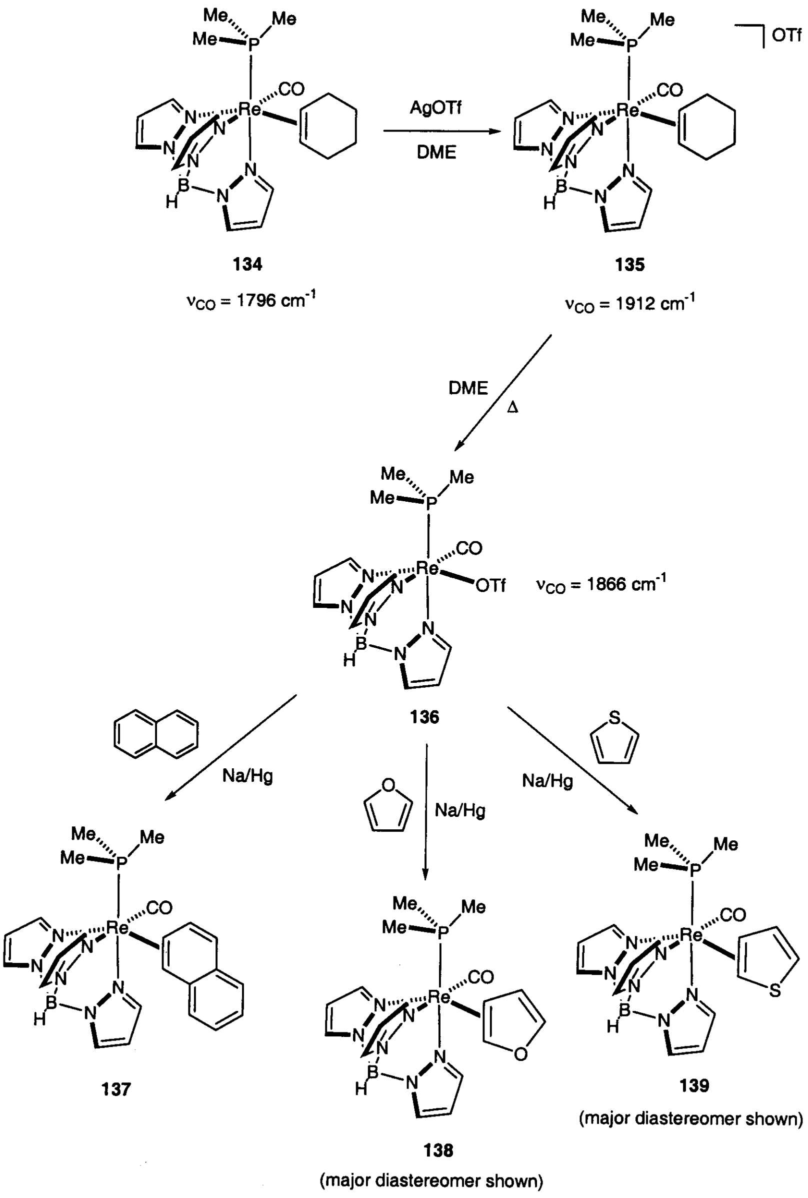


Scheme 41.

($\nu_{CO} = 1866$ cm^{-1}). After cooling to r.t., the reduction of **136** in the presence of naphthalene, furan or thiophene yields the corresponding η^2-aromatic complexes {naphthalene (**137**), 55%; furan (**138**), 81%; thiophene (**139**), 77%}.

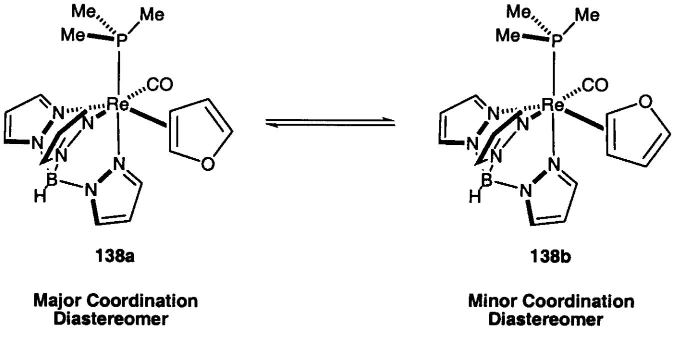
The naphthalene complex **137** demonstrates reasonable thermal stability. At r.t. as an acetone-d_6 solution, the disappearance of **137** can be monitored. Importantly, monitoring the disappearance reveals no signs of C–H oxidative addition. Rather, a quantitative ligand substitution process occurs. Thus, observing an acetone-d_6 solution of **137** reveals the appearance of resonances corresponding to the formation of free naphthalene and TpRe(CO)(PMe$_3$)(η^2-acetone) ($t_{1/2} = 5.9$ h at r.t.) (vide infra).

Notably, only a single coordination diastereomer is observed for complex **137**. Through spectroscopic studies, it was conclusively determined that for the observed diastereomer the unbound aromatic ring is oriented away from the bulky trimethylphosphine ligand. Given that the rates of interconversion between diastereomers are expected to be similar to analogous fluxional processes of [Os(NH$_3$)$_5$(η^2-naphthalene)]$^{2+}$ [14], the observation of a single diastereomer of **137** is assumed to reflect a thermodynamic preference of the {TpRe(CO)(PMe$_3$)} fragment.



Scheme 42.

In contrast to the naphthalene complex, two diastereomers (2.1:1.0 ratio) are observed for the furan complex **138a** and **138b** (Scheme 43). The furan complex is more stable than the naphthalene species and undergoes ligand exchange with acetone ($t_{1/2} \approx 7$ days at r.t.). The dependence of the rate of ligand exchange on the nature of the aromatic ligand indicates that the rate determining step in these

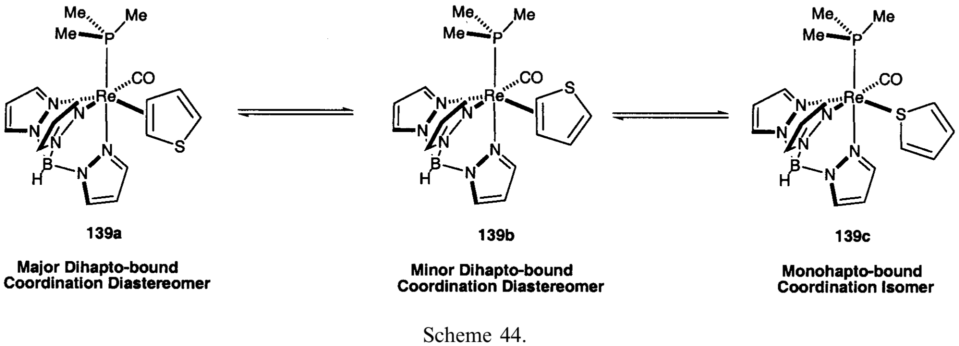


Scheme 43.

reactions is likely dissociation of the aromatic ligand. The decrease in binding selectivity upon replacing naphthalene with furan is likely explained by the small steric difference between the two enantiofaces of the furan moiety.

Unlike furan, thiophene has access to two distinct two-electron donor coordination modes. In fact, the majority of complexes with a two-electron donating thiophene ligand in the coordination sphere bind thiophene η^1 through the sulfur atom [133,134]. The {TpRe(CO)(PMe$_3$)} fragment coordinates thiophene as a mixture of three isomers (**139a**–**c**) (Scheme 44), and the deconvolution of spectroscopic features indicates the presence of two η^2-bound diastereomers and an η^1-bound isomer in a 3.2:2.0:1.0 ratio (at r.t. for **139a**:**139b**:**139c**).

An important aspect of the TpRe synthesis delineated above is the fact that the PMe$_3$ ligand can be easily changed at the Re(III) phosphine oxide step. Accordingly, the electronic and steric profile of the metal center can be significantly altered depending on the identity of this variable ligand. Analogs of TpRe(Cl)$_2$(PMe$_3$) (**133**) have been produced in our laboratory in which the trimethylphosphine has been replaced by a diverse group of alternate ligands (e.g. ^{t}BuNC, pyridine, ETPB, 1-methylimidazole and NH$_3$) [135]. Initial results with these systems indicate that the expected wide range of electronic characteristics (and the concomitant binding preferences) of the rhenium center is present depending on the ligand utilized.



Scheme 44.

Diastereoselectivity of subsequent reduction steps has also been shown to vary depending on the steric characteristics dictated by the new ligand. In addition, direct coordination of aromatic ligands from the Re(III) halide complexes has been demonstrated if the chlorides are replaced with bromides for certain ligand sets. Of more practical interest to the dearomatization methodology is the fact that electrophilic additions have been demonstrated not only for the PMe_3 system, but for other {TpRe(CO)(L)} systems as well. Accordingly, the purview of the {TpRe(CO)(L)} fragments is still being investigated due to the extremely versatile nature of the synthesis used to obtain them as well as their ultimate success as dearomatization agents.

4. Outlook and conclusions

The fruition of the TpRe systems will be complete once the full range of ligands has been obtained for binding at the Re(III) state, the scope of aromatic ligands coordinated to each of these systems has been explored and a resolved chiral dearomatization reagent has been realized. The next step will be to apply the insights gained from the rhenium systems to isoelectronic Mo(0) and W(0) fragments. Accordingly, TpMo fragments are currently being investigated in our lab. These systems offer the advantage of being less expensive and even more electron-rich (i.e. activating) than the corresponding rhenium fragments.

Ultimately, the advent of the {TpRe(CO)(L)} systems has accomplished the first major goal of developing a chiral surrogate to the pentaammineosmium(II) fragment. More importantly, the success obtained with these systems thus far has established that the methodology developed for producing dearomatization reagents from high-valent starting materials is sound. Furthermore, this synthetic strategy is compatible with the use of the readily available and convenient Tp and carbonyl ligands. Thus, the further development of rhenium as well as molybdenum and tungsten systems should provide a powerful and cost-effective addition to the arsenal of synthetic organic chemists.

Appendix A. Abbreviations

OTf^-	trifluoromethanesulfonate (triflate)
DMAc	*N*,*N*-dimethylacetamide
PPN	bis(triphenylphosporanylidene)ammonium
DME	1,2-dimethoxyethane
9BBN	9-boracyclo[3.3.1]nonane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
CAN	ceric ammonium nitrate
py	pyridine
^{t}Bupy	4-*tert*-butylpyridine

bpy	2,2′-bipyridyl
tbpy	4,4′-di-*tert*-butyl-2,2′-bipyridyl
terpy	2,2′,2″-terpyridyl
ETPB	4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane
dien	diethylenetriamine
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
MVK	methyl vinyl ketone
MMTP	1-methoxy-2-methyl-1-(trimethylsiloxy)-2-propene
Tp	hydridotris(pyrazolyl) borate
TBAH	tetrabutylammonium hexafluorophosphate

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