

# Development of $\pi$ -basic dearomatization agent : Chemistry of $\eta^2$ - coordination type reaction

Ref. *Tetrahedron* 2001, 57, 8203. *Chem. Rev.* 1997, 97, 1979. *Organometallics* 2005, 24, 1786-1798

Today's contents

- I: Introduction
- II: Design of other  $\eta^2$ -dearomatization agent
- III: Diels Alder Reaction
- VI: Cycloaddition Reaction

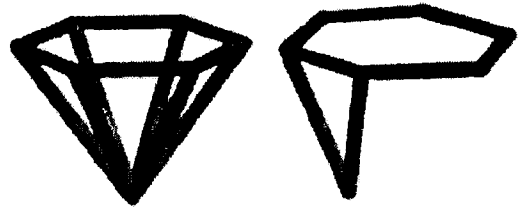
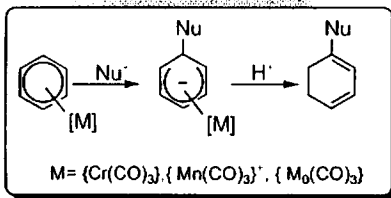


Figure1: Common coordination modes for arenes.

Scheme 1  $\eta^6$ -aromatic system



Scheme 2  $\eta^2$ -aromatic system

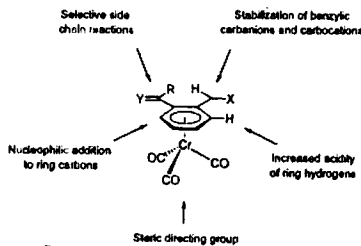
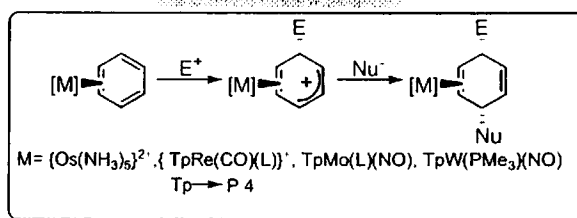
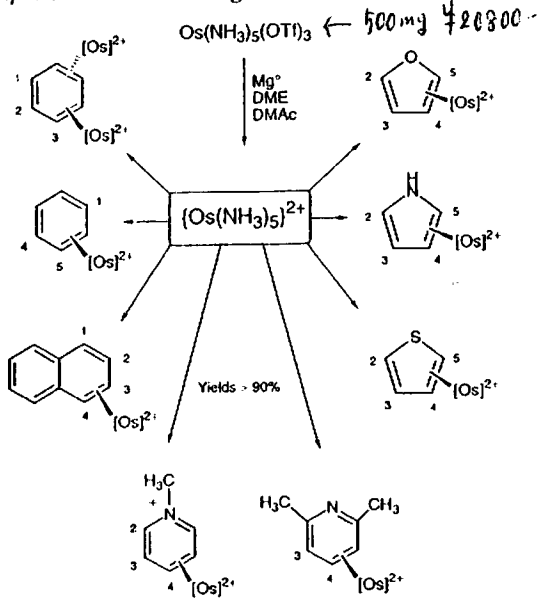


Figure 3 Changes in arene reactivity after complexation with chromium tricarbonyl.



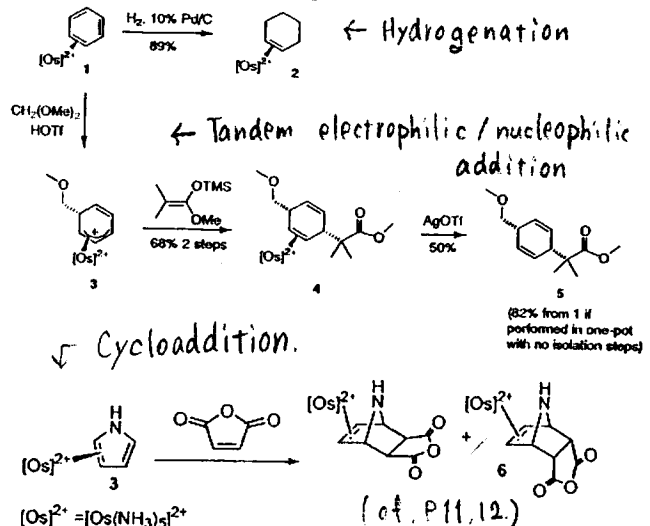
Prof. W. Dean Harman

Figure 2 A survey of pentaammineosmium(II) complex with  $\eta^2$ -bound aromatic ligands.



Scheme 3

Examples of synthetic application of the dearomatization agent pentaammineosmium(II).



# I : Introduction

For over four decades, organometallic chemists have exploited the ability of transition metals to promote otherwise inaccessible reactions of arenes.

## < The activation aromatic mode >

**$\eta^6$ -aromatic system**  
 # Most common  
 # Metal:  $\{Cr(CO)_3\}$ ,  $\{Mn(CO)_3\}^+$ ,  $\{Mo(CO)_3\}$   
 # Reactivity: Due to electron-withdrawing properties of Metal-ligand, The complex is susceptible to nucleophilic addition.

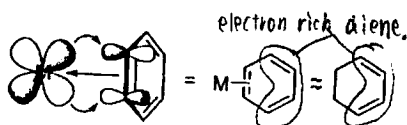


Figure 1.  $\eta^2$  coordination stabilized through  $\pi$ -donation of electron density.

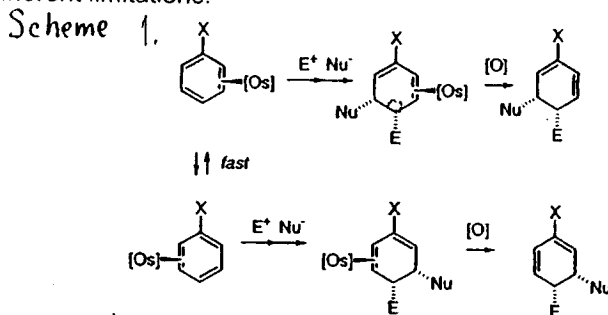
**$\eta^2$ -aromatic system**  
 # Rare. Prof. Harman have developed this system since 1987  
 # Metal:  $\{Os(NH_3)_5\}^{2+}$ ,  $\{TpRe(CO)(L)\}^+$ ,  $TpMo(L)(NO)$ ,  $TpW(PMe_3)(NO)$   
 # Reactivity: Donation of  $\pi$ -electron density from a filled d-orbital of the octahedral  $d^6$  metal into an antibonding orbital of the aromatic molecule serves to both increase and localize the electron density of the aromatic  $\pi$ -system. So, these molecules react with electrophile.  
 # Transformation examples: Scheme 3

However the pentaammineosmium(II) fragment has inherent limitations.

$\{Os(NH_3)_5\}^{2+}$  system  
 Problems: achiral, cost, toxicity



Alternatives to the pentaammineosmium(II) system  
 low cost, chiral metal center  
 $M = \{TpRe(CO)(L)\}^+$ ,  $TpMo(L)(NO)$ ,  $TpW(PMe_3)(NO)$



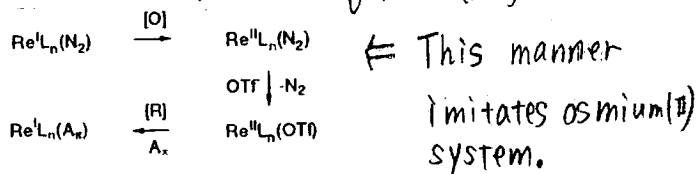
## II : Design of other $\eta^2$ dearomatization agents.

[A] Development of  $[TpRe(CO)(L)]^+$  fragment.

(II-A-1) To develop a low valent rhenium(I) complex.

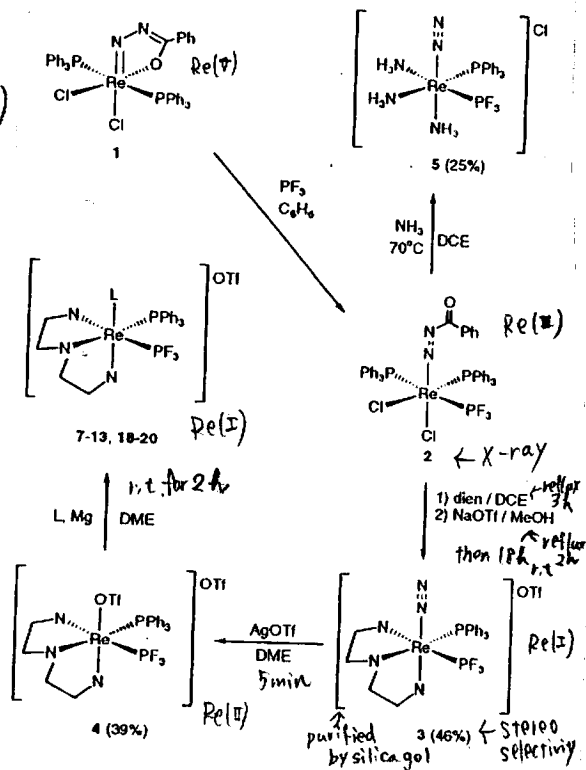
- Ref: ① Organometallics 1998, 17, 4716-4723  
 ② Inorg. Chem. 1997, 36, 3553-3558  
 ③ Inorg. Chem. 1994, 33, 3026-3027

### Scheme 0: Synthesis of $Re^I L_n(Ar)$



- The preparation of rhenium(I) dinitrogen complexes from an N-benzoylhydrazidoprecursor. This method developed by Chart.
- The complex 3 is obtained in stereo selectivity.

### Scheme 2: Reaction Scheme for Synthesis of Low-Valent Rhenium(I) Precursors Containing the $PF_3$ Ligand from (N-benzoylhydrazido-N',O)dichlorobis(triphenylphosphine)rhenium(V)



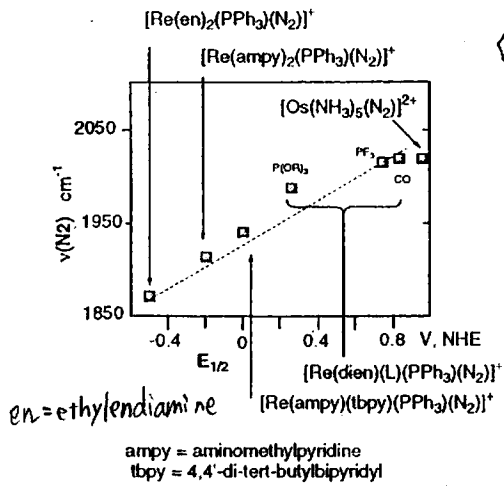


Figure 1. Correlation of electrochemical and infrared spectroscopic data for various rhenium(I) dinitrogen complexes.

↳  $\nu \text{ cm}^{-1}$   
=  $\pi$ -back bonding level  
•  $E_{1/2} \text{ (V)}$   
= Electron Potential

Table 1. Comparison of Spectroscopic, Electrochemical, and Physical Properties of the  $\{\text{Os}(\text{NH}_3)_5\}^{2+}$  and  $\{\text{Re}(\text{dien})(\text{PPh}_3)(\text{PF}_3)\}^+$  Systems

ligand	attribute	$\{\text{Os}(\text{NH}_3)_5\}^{2+ c}$	$\{\text{Re}(\text{dien})(\text{PF}_3)(\text{PPh}_3)\}^+ c$
CH <sub>3</sub> CN	$\nu(\text{CN})^b \text{ (cm}^{-1}\text{)}$	2191	2217
	$E_{1/2}^d \text{ (V)}$	-0.10	0.11
N <sub>2</sub>	$\nu(\text{NN})^b \text{ (cm}^{-1}\text{)}$	2037	2033
	$E_{1/2}^d \text{ (V)}$	0.98	0.86
H <sub>2</sub>	H-H(calcd) (Å)	1.17	1.31
CpH	binding mode	$\eta^2$	$\eta^2$
	$E_{1/2}^d \text{ (V)}$	0.65	0.51
	electrophilic addition	yes	yes
arenes	binding mode	$\eta^2$	none
thiophene	binding mode	$\eta^2$	S

<sup>c</sup> CH<sub>3</sub>CN; TBAH. <sup>b</sup> KBr. <sup>c</sup> OTf<sup>-</sup> counterion. <sup>d</sup> DMAc; TBAH (NHE).

These are problems.  
→ Steric differences

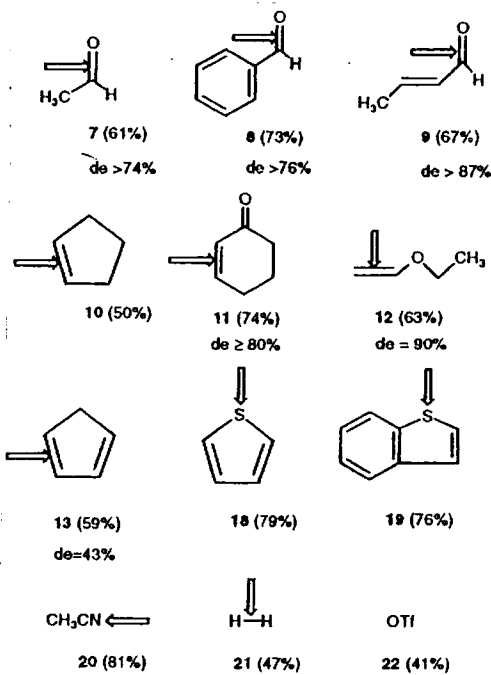
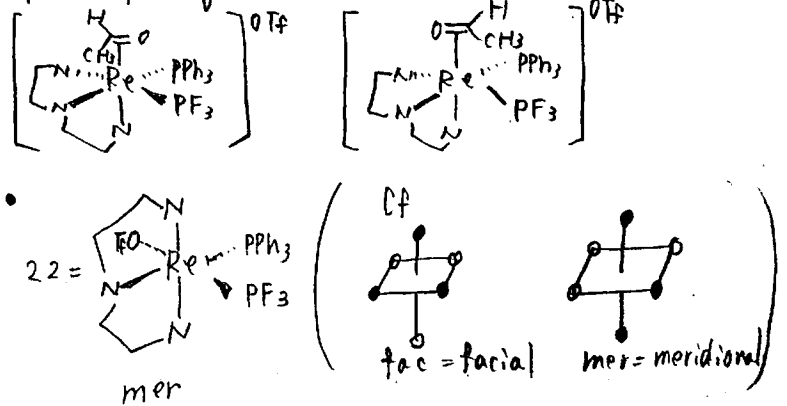


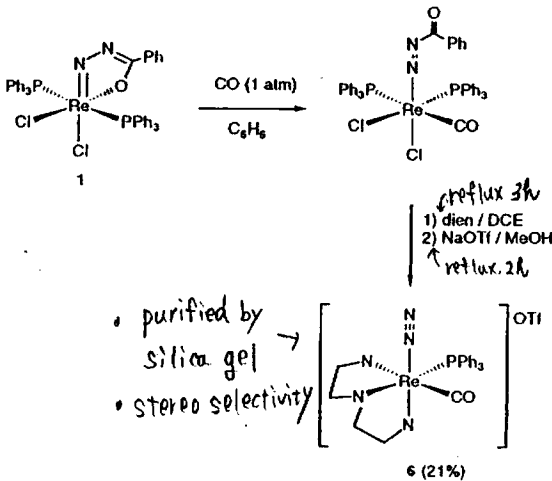
Figure 2. Scope of ligands which coordinate to the  $[\text{Re}(\text{dien})(\text{PPh}_3)(\text{PF}_3)]^+$  fragment with binding site, yield, and diastereomeric excess (where applicable).

↳ Major diastereo isomer is shown.  
• Example of diastereo isomer

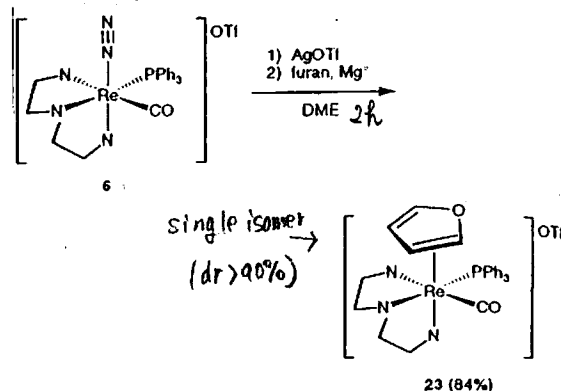


↳ CO: smaller ligand than PF<sub>3</sub>  
• fac- $\{\text{Re}(\text{dien})(\text{PPh}_3)(\text{CO})\}^+$  fragment failed to bind a range of aromatic ligands or activate furan toward novel reactions.  
→ This is a problematic point.

Scheme 1 Synthesis of fac-[Re(N<sub>2</sub>)(dien)(PPh<sub>3</sub>)(CO)](OTf) from (N-Benzoylhydrazido-N',O)-dichlorobis(triphenylphosphine)rhenium(V)



Scheme 2 Synthesis of an  $\eta^2$ -Furan Complex from fac-[Re(N<sub>2</sub>)(dien)(PPh<sub>3</sub>)(CO)](OTf)



• In these fragment design, it is important to consider electron properties and a steric profile.

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(II-A-2) To search for the other ligand.

Ref: ① Organometallics 2000, 2428-2432

② J. Am. Chem. Soc. 1998, 120, 8747-8754

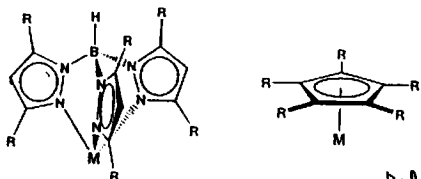
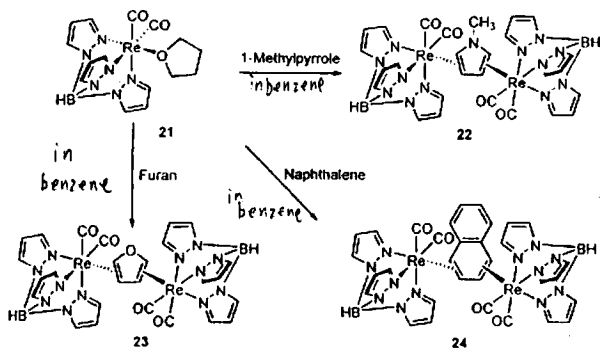


Figure 1. Hydridotris(pyrazolyl)borate ligand and cyclopentadienyl ligand. Cone angle for Cp = 150° (R = H), 182° (R = Me) and Tp = 262° (R = H), 276° (R = Me).<sup>3</sup>

Scheme 1. Formation of Binuclear  $\eta^2$  Complexes from  $TpRe(CO)_2(THF)$



< Characteristic of Hydridotris(pyrazolyl) borate ligand (Tp) >

- \* anionic six-electron donor
- \* an analogue of cyclopentadienyl (Cp)

- \* the sterically encumbering nature
- \* Tp  $\rightarrow$  hard nitrogen  $\delta$  donors

Cp  $\rightarrow$  relatively soft  $\pi$  donation.

- \* Tp ligand enforces an octahedral geometry.

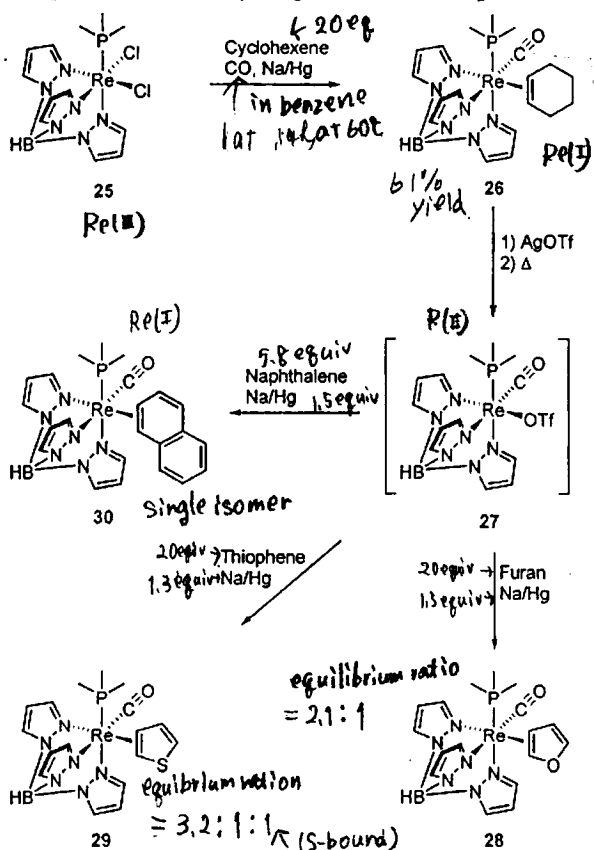


- Binuclear  $\eta^2$  Complexes were obtained
- $\{TpRe(CO)_2\}$  fragment was not sufficiently electron-rich to prevent its disproportionation. But  $\{TpRe(CO)_2\}$  with aromatic molecules was variable.

$\Rightarrow$  The pursuit of complexes of the type  $\{TpRe(L)(CO)\}$  (L = more  $\delta$ -donating and less  $\pi$ -withdrawing)

(II-A-3) Synthesis of the type  $\{TpRe(L)(CO)\}$ .

Scheme 2 Synthesis of  $TpRe(PMe_3)(CO)(\eta^2\text{-furan})$ ,  $TpRe(PMe_3)(CO)(\eta^2\text{-thiophene})$ , and  $TpRe(PMe_3)(CO)(\eta^2\text{-naphthalene})$  Complexes



Ref: ① J. Am. Chem. Soc. 1999, 121, 6499-6500

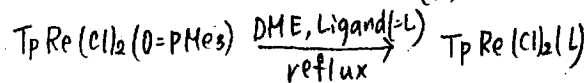
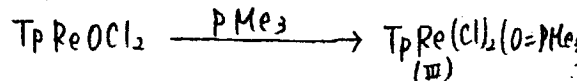
② Organometallics 2000, 19, 728-740

- $\Rightarrow$  \*  $PMe_3$ : more electron-donating
- \* The points of the synthesis of  $TpRe(PMe_3)(CO)(\eta^2\text{aromatic})$  complexes.

- 25 Re(III)  $\xrightarrow{\text{directly}}$  28, 29, 30 Re(I) the aromatic products are not stable under the thermal conditions required for halide loss.

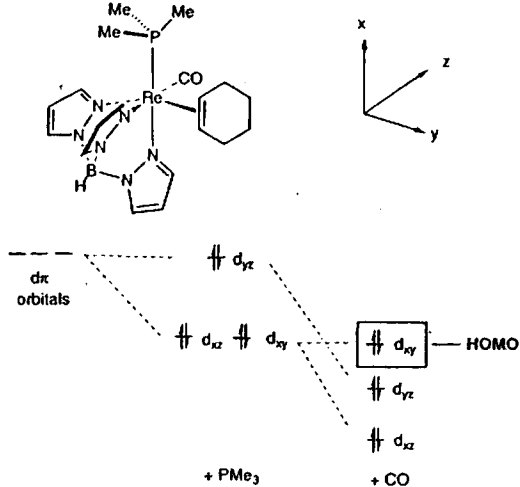
- 26 Re(I)  $\xrightarrow{\text{directly}}$  28, 29, 30 Re(I) Re(I) oxidation state proved to be substitution inert.

- 25:  $NaReO_4 \xrightarrow[EtOH, reflux, 2h]{KTP, conc HCl} TpReOCl_2$  (v)

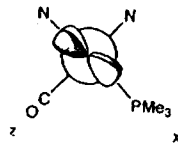


\* Stereochemical feature of the  $\{TpRe(CO)PMe_3\}^+$  fragment

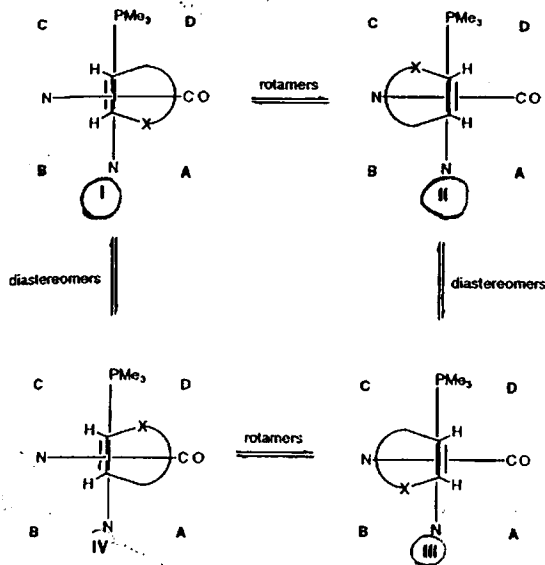
Scheme 1. Qualitative Molecular Orbital Diagram for  $TpRe(CO)(PMe_3)(\eta^2\text{-cyclohexene})$  (7) and Depiction of the  $d_{xy}$  HOMO



- $d_{xy}$ -back-bonding with  $PMe_3$  would lower the energy of the  $d_{xy}$  and  $d_{yz}$  orbitals.
- $d_{xy}$ -back-bonding with  $CO$  would lower the energy of the  $d_{xz}$  and  $d_{yz}$  orbitals
- Spectrochemical series  
 $I < Br < Cl < F < OH < C_2O_4^{2-} < H_2O < NCS^- < py < NH_3 < en < bpy < O\text{-phen} < NO_2^- < CN^- < CO$
- The  $C=C$  bond is aligned parallel to the  $Re-P$  bond.



Scheme 2. Stereochemical Analysis for the System  $TpRe(CO)(PMe_3)(\eta^2\text{-L})$  (where L is an olefinic or aromatic molecule)

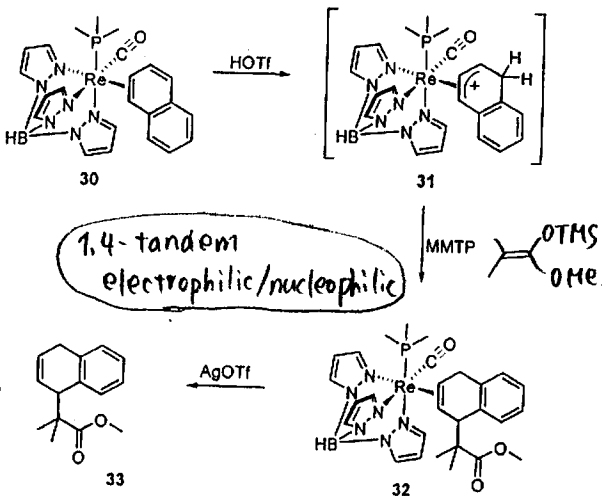


- more stable I, IV > II, III less stable (sterically imposing pyrazolyl ring)

I ⊕ IV  
 The combination of electronic and steric factors.

L =  $PMe_3$   
 The  $PMe_3$  group is large group  
 → I > IV (The steric factor)

Scheme 3. Activation of Naphthalene through  $\eta^2$  Coordination to the Second-Generation  $\{TpRe(PMe_3)(CO)\}^+$ -Basic Metal Fragment



- The  $\{TpRe(PMe_3)(CO)\}^+$  was first fragment after pentaammineosmium (I) that was shown to activate aromatic molecules toward electrophilic addition reactions through  $\eta^2$  coordination.

(The problems of this system)

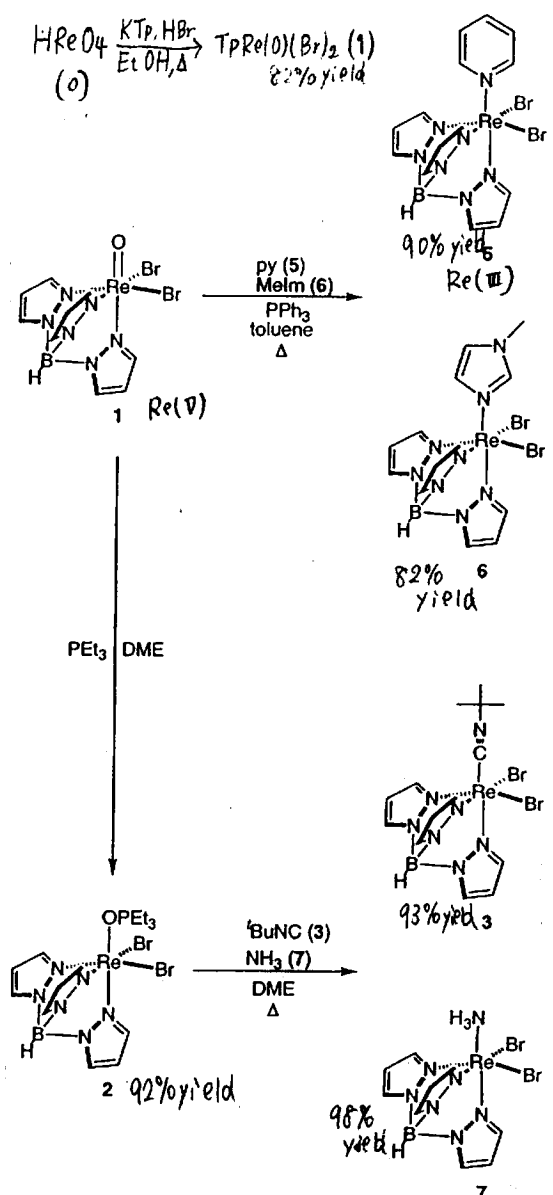
This fragment failed to form stable  $\pi$ -complexes with benzenes and nitrogenous heterocycles.

↓  
 With varying electron density, several other  $TpRe(L)(CO)$  fragments were synthesized.

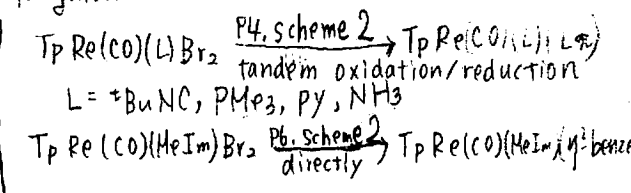
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(II-A-4) Achievement of the Second Generation Agents (Ref: Organometallics 2001, 20, 3661-3671)

Scheme 1. Synthesis of Re(III) Precursors (3, 5, 6, 7)



• Synthesis of Re(I)  $\eta^2$ -Aromatic Complexes from Re(III)-fragment



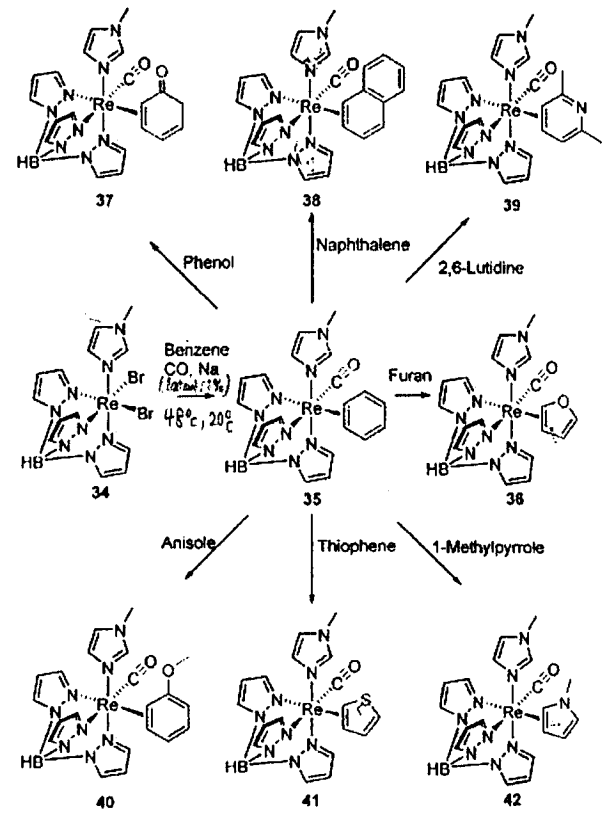
•  $\text{TPRe}(\text{CO})(\text{MeIm})(\eta^2\text{benzene})$  (35)

- stable at 25°C under dinitrogen for months with no sign of decomposition.
- In solution, benzene ligand is labile.

→ compound (35) is a useful precursor for a variety of other aromatic complexes via a ligand substitution under mild conditions. (cf. 16th, 25°C)

- $\text{TPRe}(\text{CO})(\text{L})(\text{L}\pi)$
- $\text{L} = \text{tBuCN, py}$  :  $\text{L}\pi =$  naphthalens, thiophenes, furan
  - $\text{PMe}_3$  : X benzene, pyrrole
  - $\text{L} = \text{NH}_3$  :  $\text{L}\pi =$  naphthalene only
  - $\text{L} = \text{MeIm}$  :  $\text{L}\pi \Rightarrow$  scheme 2
  - X Halogenated benzene pyridine

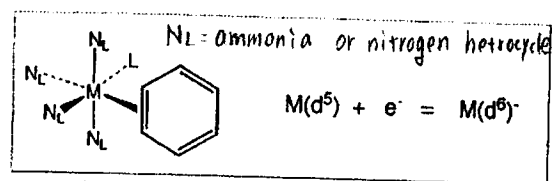
Scheme 2.  $\eta^2$  Complexation of Aromatic Molecules by the Metal Fragment  $\{\text{TPRe}(\text{MeIm})(\text{CO})\}$ .



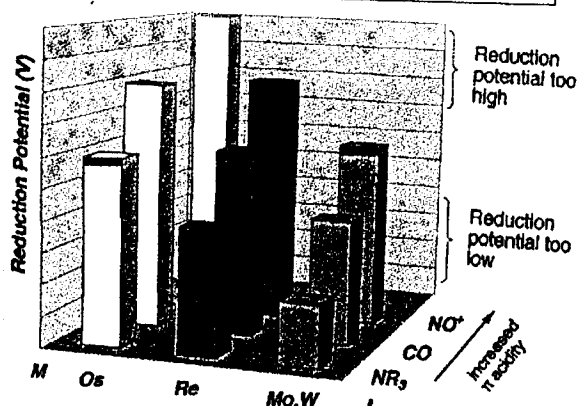
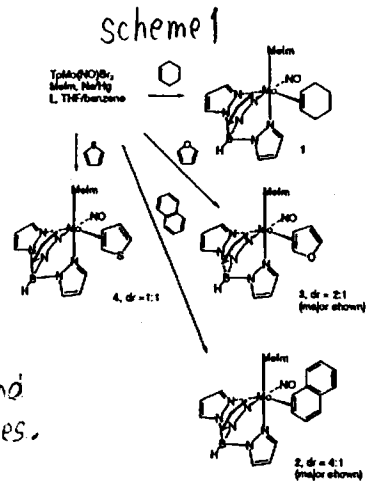
- $\text{TPRe}(\text{CO})(\text{L})(\text{L}\pi) \Rightarrow \text{L}$ : various ligand.
- A new class of  $\eta^2$ -aromatic systems have been synthesized that allows systematic adjustment of electronic and steric properties.

- advantages over the  $\{\text{Os}(\text{NH}_3)_5\}^{2+}$  fragment
- less expensive
  - Soluble in wider range of solvents.
  - chiral
  - purified by common chromatographic purification techniques.

[B] Design of other  $\eta^2$  dearomatization agents: VI group.  
 (II-B-1) Activation of Aromatic Molecules by VI group  $\pi$ -Base.



Ref) ① J. Am. Chem. Soc. 2003, 123, 2024-2023  
 ② Organometallics 2003, 22, 4244-4256



•  $\{TpMo(MeIm)(NO)\}$  failed to form stable  $\eta^2$  complexes with benzenes and nitrogenous heterocycles.

•  $\{TpW(NO)(PMe_3)\}$  fragment bind various aromatic molecules.

Scheme 2 Synthesis of  $TpW(PMe_3)(NO)(\eta^2\text{-aromatic})$  Complexes

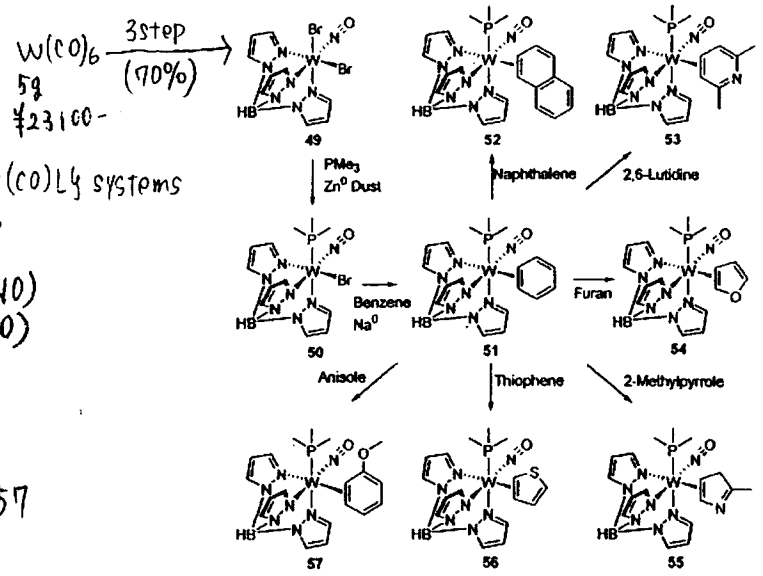


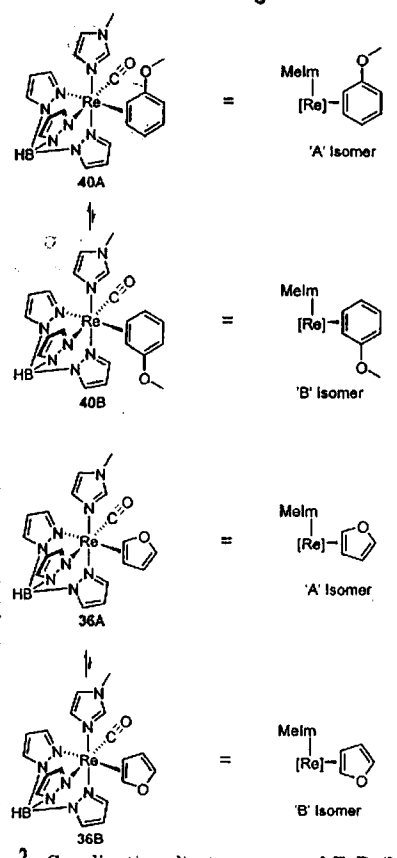
Figure 1. Reduction potentials of  $d^6$  metal complexes as a function of ligand identity.

Lessons learned in the development of  $\{TpRe(CO)L\}$  systems were applied to group 6 transition metals. (cf. P3 Figure 1)

- Mo:  $CO \rightarrow NO = TpMo(MeIm)(NO)$
  - W:  $CO \rightarrow NO = TpW(PMe_3)(NO)$
- Stronger  $\pi$  acid

\* Coordination Diastereomer.

Ref, J. Org. Chem. 2004, 69, 2257



The selectivity of diastereomer depends on the combination of electronic and steric factors.

- electronic factor:  $\pi$ -back-bonding interaction between  $\pi^*$  orbital of aromatic molecule and metal centered  $HO(L)O$ .
- Steric factor: steric hindrance of L (L = MeIm,  $PMe_3$ , py, NHa)

Smaller L  $\rightarrow$  favoring the A diastereomer  
 larger L  $\rightarrow$  favoring the B diastereomer  
 complex having smaller bond aromatic ligands  $\rightarrow$  low A:B ratio  
 complex having larger bond aromatic ligands  $\rightarrow$  higher A:B ratio

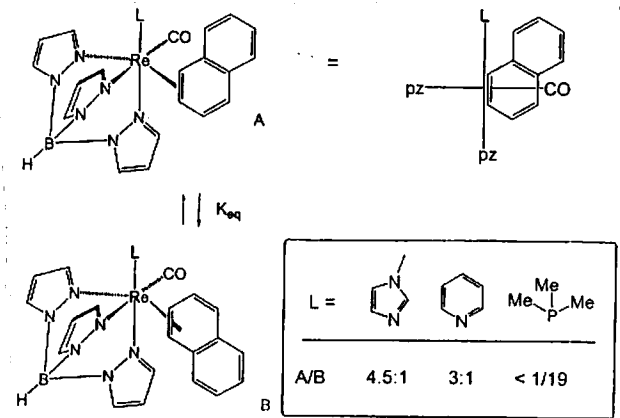


Figure 2. Coordination diastereomers of  $TpRe(MeIm)(CO)(5,6-\eta^2\text{-anisole})$  and  $TpRe(MeIm)(CO)(3,4-\eta^2\text{-furan})$ .

FIGURE 3. Coordination diastereomers of rhenium naphthalene complexes.

8/12 [C] Aspect of  $TpRe(L)(\eta^1\text{-acid})(\eta^2\text{-aromatic})$  complex

(II-C-1) Resolution of Dearomatization agent : chiral control

Ref: J. Am. Chem. Soc. 2002, 124, 15099 - 15103 / Organometallics 2006, 20, 3876-3883

The  $TpRe(L)(\eta^1\text{-acid})$  fragment has stereogenic metal center.

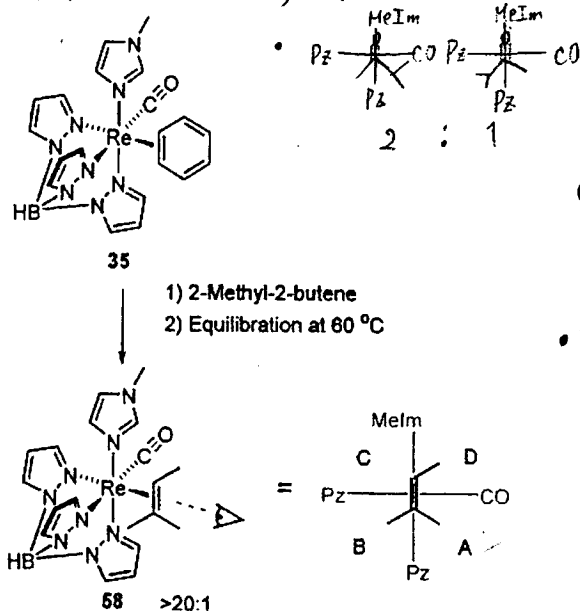


Figure 1. Thermodynamically favored orientation of the alkene in  $TpRe(MeIm)(CO)(\eta^2\text{-2-methyl-2-butene})$  and the corresponding quadrant representation.

could not be isolated or observed in situ by <sup>1</sup>H NMR.

The steric hindrance in the quadrants increases in the order  $D < A < B < C$ .

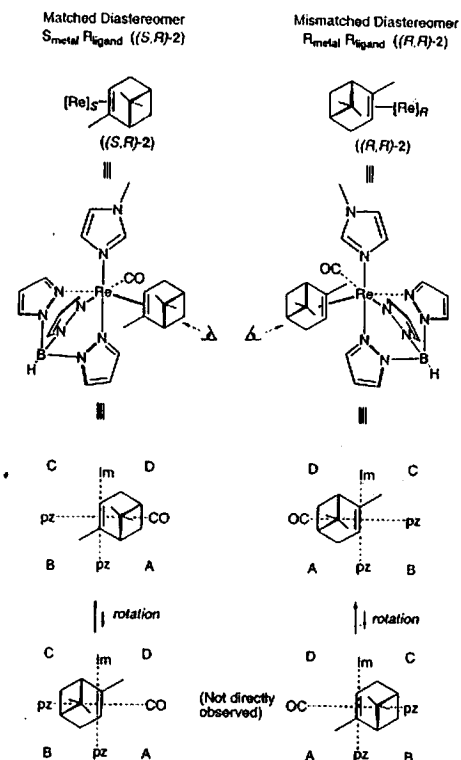
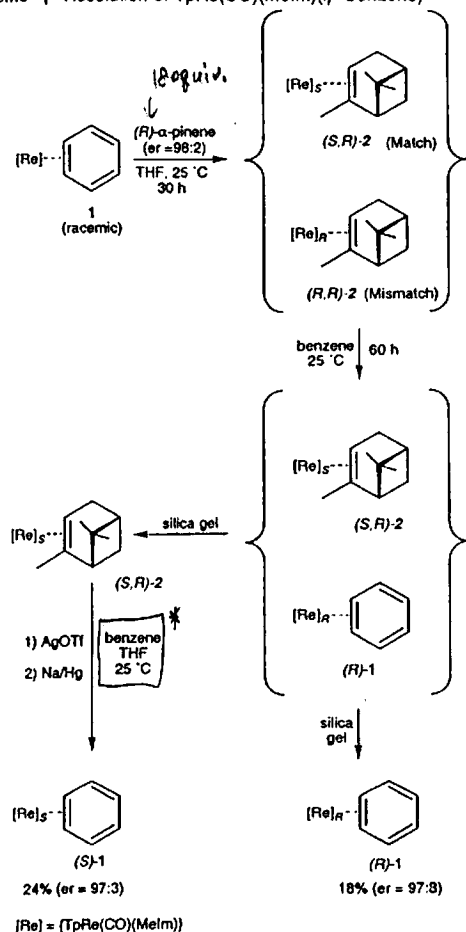


Figure 2 Match ((S,R)-2) and mismatch ((R,R)-2) diastereomers of the (R)- $\alpha$ -pinene complex.

Scheme 1 Resolution of  $TpRe(CO)(MeIm)(\eta^2\text{-benzene})$



\* In the presence of only benzene solvent, racemic mixture of 1 are obtain. The putative THF complex is sufficiently inert that racemization does not occur.

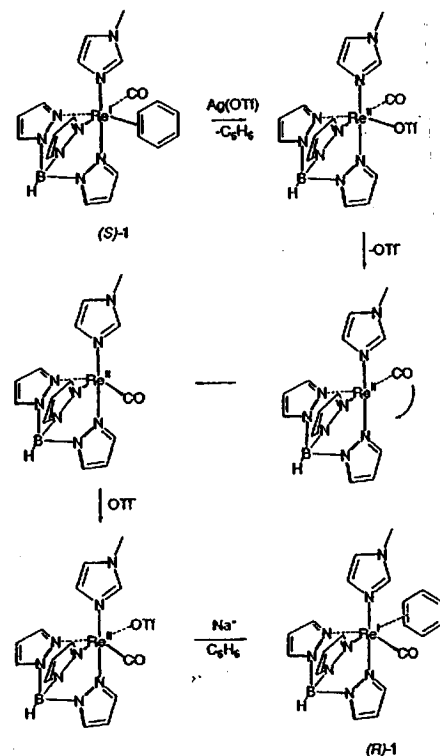


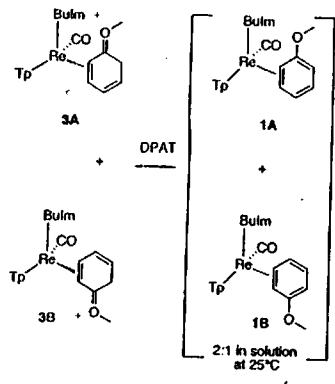
Figure 3 Racemization of  $TpRe(CO)(MeIm)(OTf)$ .



(II-C-2) Solid-state control of Diastereomers.

Ref: J. Am. Chem. Soc. 2004, 126, 785-789

Scheme 1



DPAT = diphenyl ammonium triflate

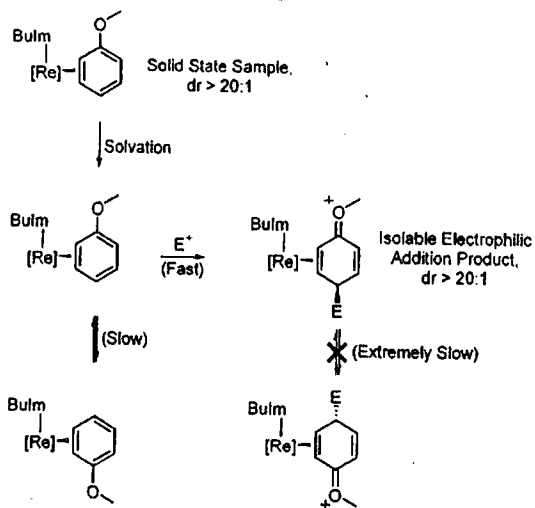
\* Equilibrium ratios are typically low (<5:1)

The associated isomerization barriers, ranging from 10 to 23 kcal/mol, are too small to make any solution based separation of diastereomers practically.

\* When solid sample 1 was dissolved at -60°C in the presence of the acid, the 3A:3B ratio of the protonated products was >20:1.

→ The utilized solid sample of 1 had a much higher diastereomeric ratio than that was observed in solution under equilibrium control.

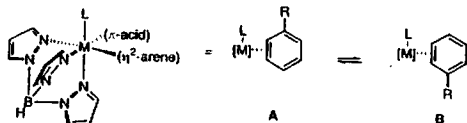
Scheme 2 Highly Diastereoselective Additions to TpRe(Bulm)(CO)(η<sup>2</sup>-anisole) Complexes Based on Diastereoselectivity Present in Solid-State Samples



\* The isomerization was not observed in sufficiently low temperature.

\* Once TpW(π-acid)(L)(η<sup>2</sup>-arene) complexes are protonated, heterofacial isomerization becomes sufficiently slow at room temperature such that no conversion is observed over many hours in solution.

Table 1.<sup>a</sup>



Facial diastereomer designated by orientation of arene substituents with respect to L.

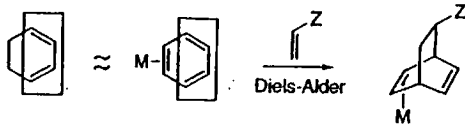
complex	equilibrium A:B <sup>b</sup>	initial A:B <sup>c</sup>	protonated A:B <sup>d</sup>	crystal structure	
				isomer	space group
[MeImRe]-anisole (4)	2:1	2:1 <sup>e</sup>	<20:1		
MeImRe]-3-methylanisole (5)	2:1	2:1 <sup>e</sup>	<1:20	A	P2(1)/n
[MeImRe]-naphthalene (6)	4.5:1	>20:1 <sup>f</sup>	>20:1	A	P2(1)/n
[BulmRe]-anisole (1)	2:1	>20:1 <sup>e</sup>	>20:1	A	P-1 (No. 2)
[BulmRe]-3-methylanisole (7)	2:1	12:1 <sup>h</sup>	>20:1	A	P-1
[BulmRe]-4-methylanisole (8)	1:2	1:12 <sup>h</sup>	1:6	A	P-1
[BulmRe]-naphthalene (9)	3.5:1	>20:1 <sup>e</sup>	>20:1	A	P-1
[PyRe]-naphthalene (10)	3:1	>20:1 <sup>e</sup>	10:1	A	C2/c (No. 15)
[PMe <sub>3</sub> Re]-naphthalene (11)	<1:20	<1:20 <sup>g</sup>	<1:20	A	
[MeImMo]-naphthalene (12)	4:1	>20:1 <sup>e</sup>	>20:1	A	P2(1)/n
PM <sub>3</sub> W]-anisole (13)	3.5:1	>20:1 <sup>e</sup>	>20:1	A	P2(1)/c

<sup>a</sup> [M] = {TpM(π-acid)}, [MeImRe] = {TpRe(CO)(MeIm)}, [BulmRe] = {TpRe(CO)(Bulm)}, [PyRe] = {TpRe(CO)(Py)}, [PMe<sub>3</sub>Re] = {TpRe(CO)(PMe<sub>3</sub>)}, [MeImMo] = {TpMo(NO)(MeIm)}, [PM<sub>3</sub>W] = {TpW(NO)(PMe<sub>3</sub>)}. <sup>b</sup> Ratio of coordination diastereomers observed in equilibrated solutions at ambient temperature. <sup>c</sup> Highest ratio of coordination diastereomers observed. <sup>d</sup> Highest ratio of protonated coordination diastereomers observed. <sup>e</sup> Complete solvation could not be effected at low temperature. <sup>f</sup> Acid-free CD<sub>2</sub>Cl<sub>2</sub> at -20 °C. <sup>g</sup> Acid-free CD<sub>2</sub>Cl<sub>2</sub> at -80 °C. <sup>h</sup> Acetone-d<sub>6</sub> at -60 °C. <sup>i</sup> Acetone-d<sub>6</sub> at ambient temperature. <sup>j</sup> Acetonitrile-d<sub>3</sub> at ambient temperature.

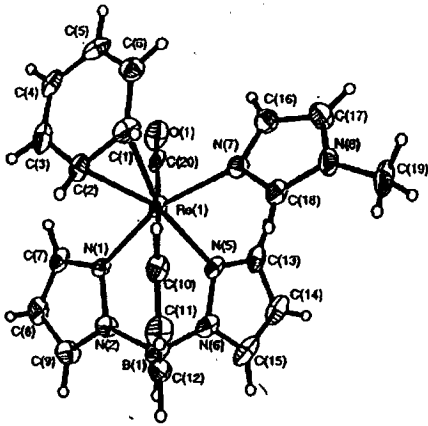
# 1/2 (III) Diels-Alder Cycloaddition with Benzene and a Maleimide

Ref: ① J. Am. Chem. Soc. 2001, 123, 10756-10757 (Re)

② J. Org. Chem. 1994, 59, 6506-6507



\* Simple aromatic molecules are rarely employed as a dien in Diels-Alder reactions due to their inherent aromatic stability. A thermodynamic barrier of 20-40 kcal/mol must be overcome in order to induce such reactivity from benzene.



\* Coordination environment, both osmium and rhenium can form stable complexes with arenes in which only two of six carbons are coordinated. Once complexed in dihapto fashion, the uncoordinated portion of the arene more closely resembles a conjugated diene.

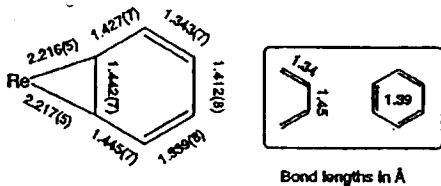
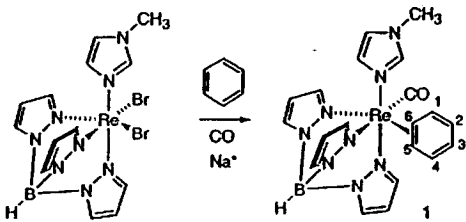


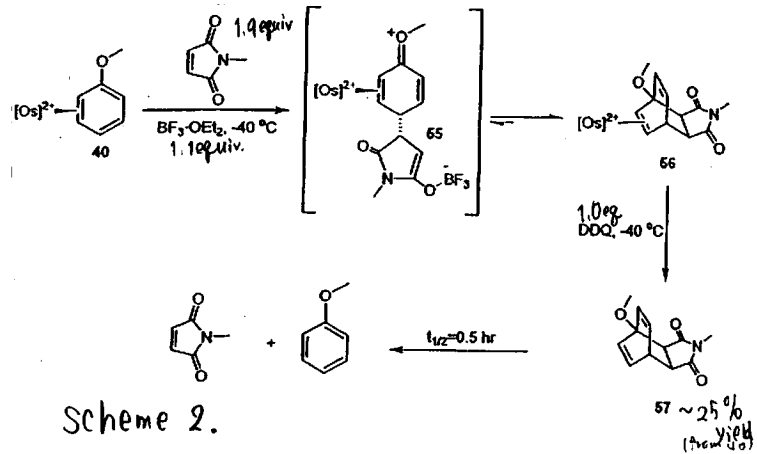
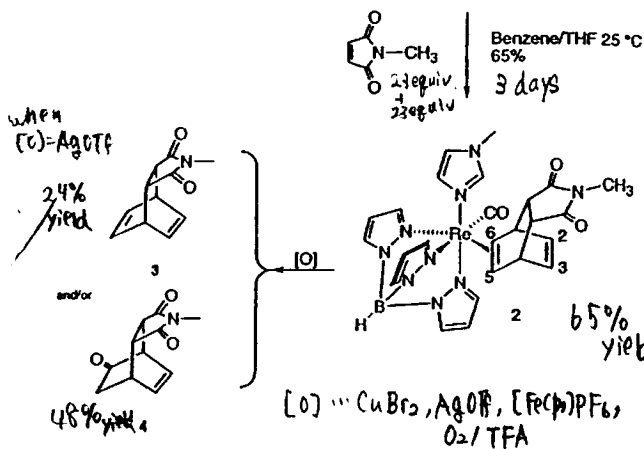
Figure 1.

Scheme 1. Rhenium-Promoted Diels-Alder Cycloaddition Reaction with Benzene and a Maleimide



\* The complex  $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-benzene})]^{2+}$  does not react with N-Methylmaleimide.

\* The anisole complex 40 does react with NMM in the presence of  $\text{BF}_3$  to yield a para-substituted anisolum resulted from Michael addition. The cyclo adduct complex forms through nucleophilic ring closure of  $\text{BF}_3$ -enolate, resulting in formal [4+2] cyclo adduct.



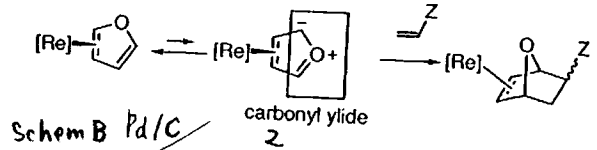
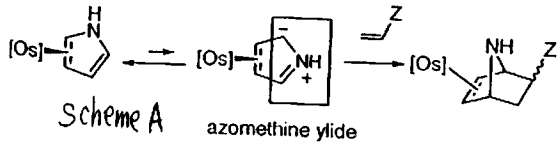
Scheme 2.

⇒ The difference in reactivity of this Diels-Alder Reaction with NMM is attributed to the greater  $\pi$ -donating ability of the  $\text{Re}(\text{I})$  fragment compared to that of the osmium system.

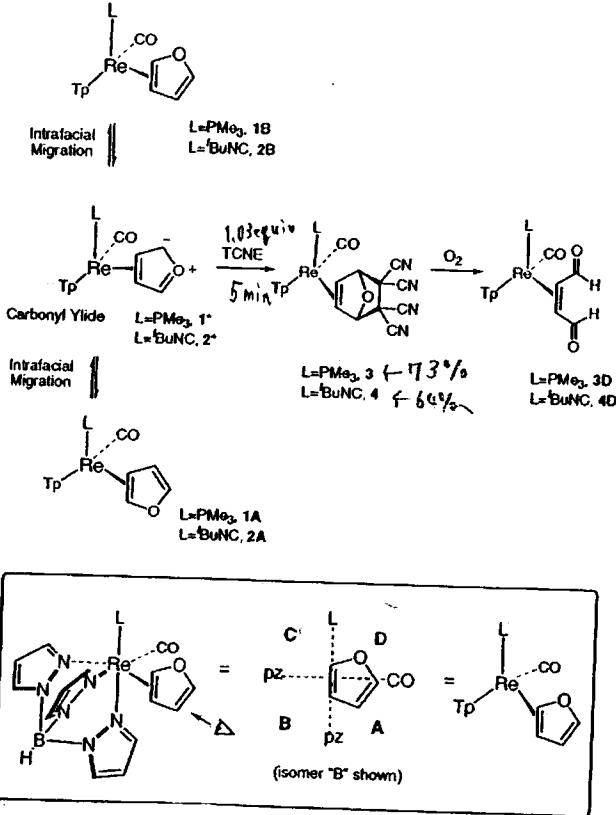
# (IV) Cycloaddition Reaction of Dinapto-Coordination Furans

1/12

Ref: J. Am. Chem. Soc. 2002, 124 17395-17404



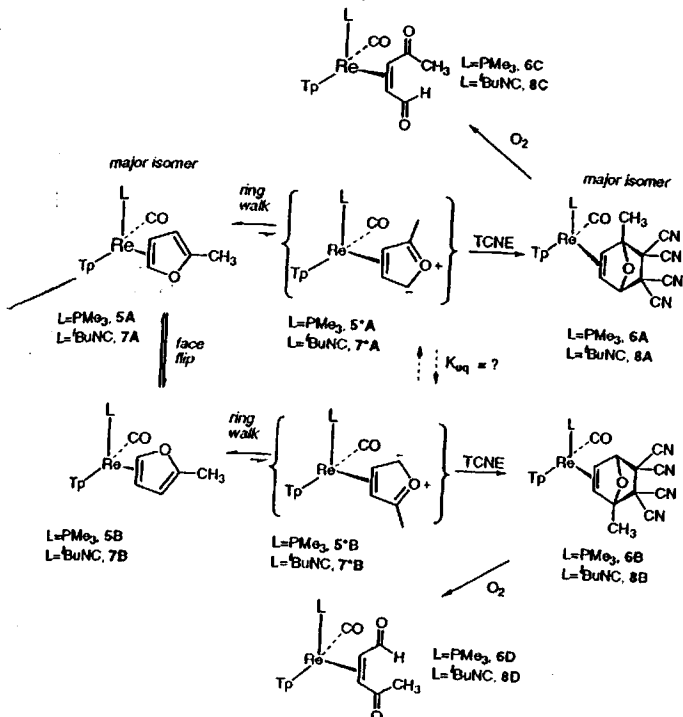
**Scheme 1.** Syntheses of 7-Oxabicyclo[2.2.1]heptene Complexes and Their Oxidation to Enedials



- \* The furan complex of pentaammineosmium(II) shows no reactivity with maleicanhydride over a 10 day period (20°C).
- \* The more electron-rich rhenium systems could raise the energy of the HOMO for the putative 3,4-η<sup>2</sup>-furan intermediate, a carbonyl ylide, to such an extent that dipolar cycloaddition reaction would become accessible.

- \* The tetranitrile cycloadducts are air sensitive.
- \* The phosphine complex\* reacted with TCNE at a rate approximately 6 times faster than did the isonitrile analogue 2\*.
- \* The rhenium furan and 2-methylfuran complexes undergo cycloadditions with TCNE that are essentially complete in < 5 min.

**Scheme 2.** Syntheses of 1-Methyl-7-oxabicyclo[2.2.1]heptene Complexes and Their Oxidation



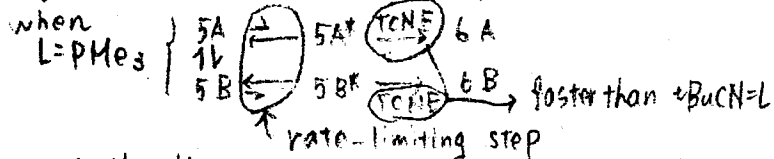
## Diastereomer Ratios

L=PMe<sub>3</sub> 5A:5B = 2.1:1 → 6A:6B = 1.8:1 Total yield 67%

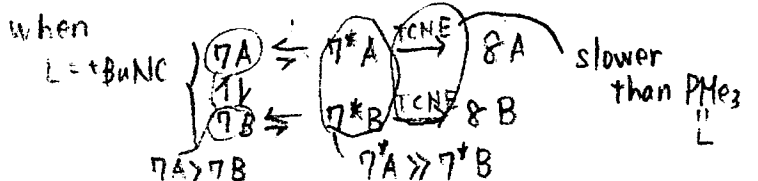
L=+BuNC 7A:7B = 4.9:1 → 8A:8B = 27:1 Total yield 69%

why?

The coordination diastereomer ratios for the products will be related to the ratio of the carbonyl ylides and to the relative rates of cycloaddition of these intermediates with TCNE.



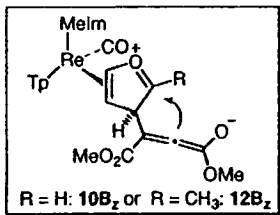
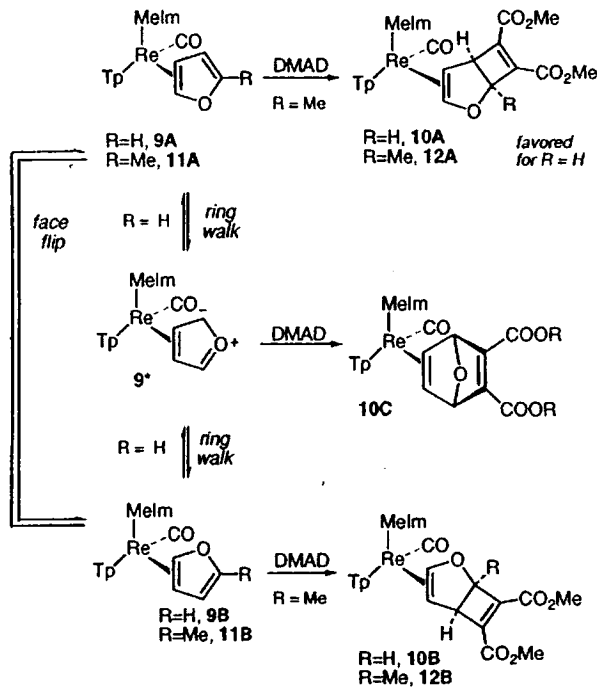
→ the diastereomer ratio for furan coordination would be similar to cycloadduct dr.



→ If cycloaddition is sufficiently slow such that the carbonyl ylides are able to equilibrate, then the ratio of furan complexes 7A and 7B would be irrelevant and the ratio of 7A\* to 7\*B, which is expected to heavily favor 7A\* would determine the ratio of cycloadducts.

12/12

**Scheme 3.** The Reaction of the Furan-Imidazole Complexes 9 and 11 with DMAD



\* Electron rich Metal TpRe(CO)(L)  
L=MeIm > L=PMe<sub>3</sub> > L=<sup>+</sup>BuNC

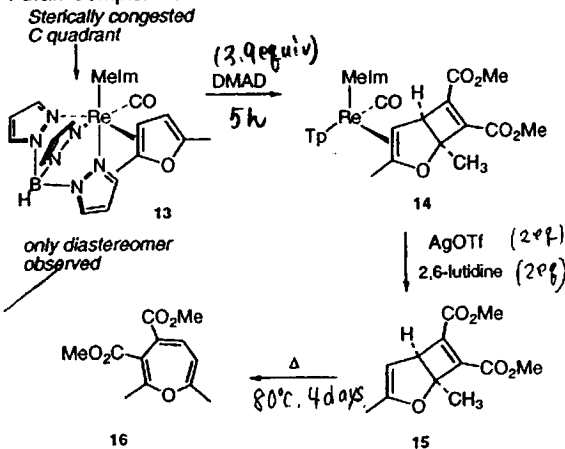
\* Diastereomer ratio

R=H : 10A:10B:10C = 10:1:18

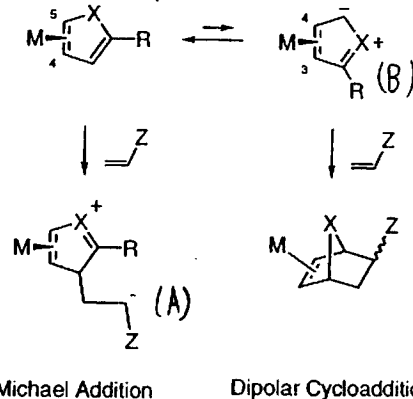
10C is major isomer

R=CH<sub>3</sub> : 12A:12B = 1:1

**Scheme 4.** Synthesis of a 2-Oxabicyclo[3.2.0]hepta-3,6-diene from Furan Complex 13



**Scheme 5.** Michael Addition/1,3-Dipolar Cycloaddition Reaction Manifold for η<sup>2</sup>-Furan Complexes



\* Michael Addition pathway was favored by stabilizing the zwitterionic intermediate, either through solvent interactions, Lewis acids, or functional group effect.

\* This manifold can be viewed as a competition between a dipolar cycloaddition of a 3,4-η<sup>2</sup> furan complex and a Michael reaction of more stable but less reactive 2,3-η<sup>2</sup> isomer

\* The presence of a methyl group at C2 apparently sufficiently stabilizes the zwitterionic intermediate through hyperconjugation, so that the dipolar cycloaddition pathway is completely pre-empted by the Michael addition.

