



# SYNTHESES OF ARCHITECTURALLY NOVEL METALLAHETEROCYCLES VIA ALKENE and ALKYNE METATHESIS (from insulated molecular wires to molecular gyroscopes)

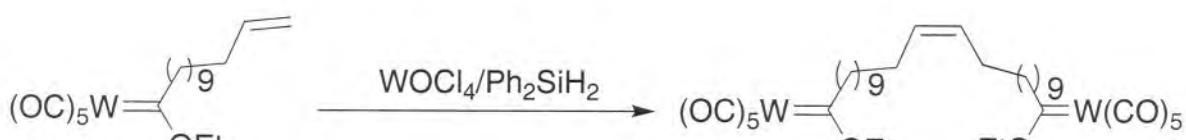
Eike Bauer,  
Takamori Shima,  
J. A. Gladysz,  
and other coworkers

Institut für Organische Chemie  
Universität Erlangen-Nürnberg

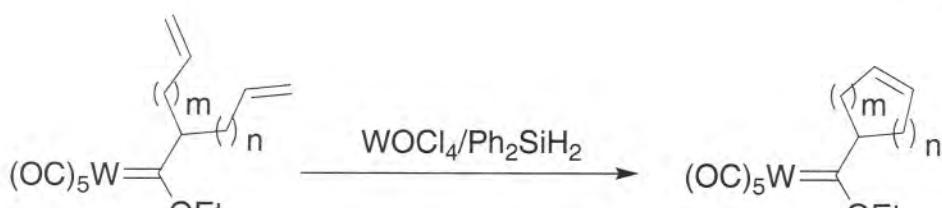
XXI. European Colloquim on  
Heterocyclic Chemistry  
Sopron, Hungary  
September 13, 2004

metathesis catalyst, Bavarian style

## FIRST EXAMPLES, C=C METATHESIS IN METAL COORDINATION SPHERES



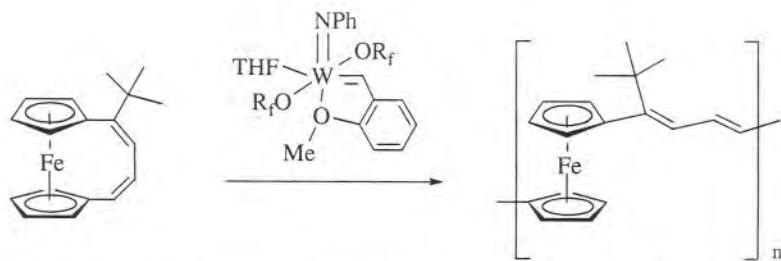
22%



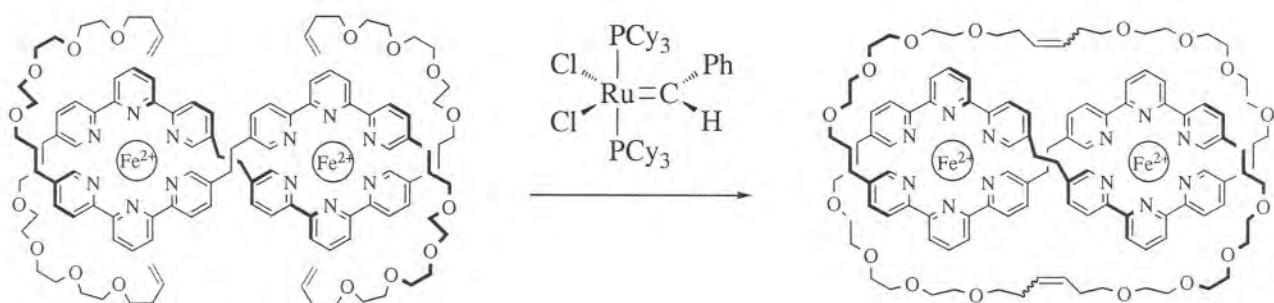
m/n = **a**, 1/1, 27%  
**b**, 1/2, 41%

TON < 4

# SOME EARLY EXAMPLES, C=C METATHESIS IN METAL COORDINATION SPHERES



R.W. Heo, F.B. Somoza, T.R. Lee, *J. Am. Chem. Soc.* **1998**, *120*, 1621

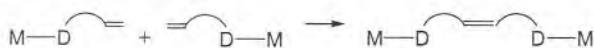


G. Rapenne, C. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1999**, *121*, 994

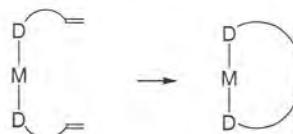
## TOWARDS a RATIONAL DEVELOPMENT of the FIELD: CONCEPTUAL TYPES of C=C METATHESIS in METAL COORDINATION SPHERES

charged/neutral complexes; coordinatively saturated/unsaturated complexes; octahedral/square planar/etc. complexes

### A: Joining Two Complexes



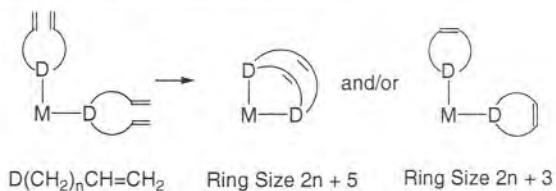
### D: Cyclization Between Two trans Ligands



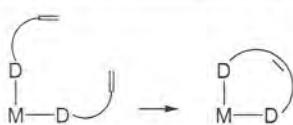
### B: Cyclization Within One Ligand



### E: Polycyclizations Involving Two cis Ligands



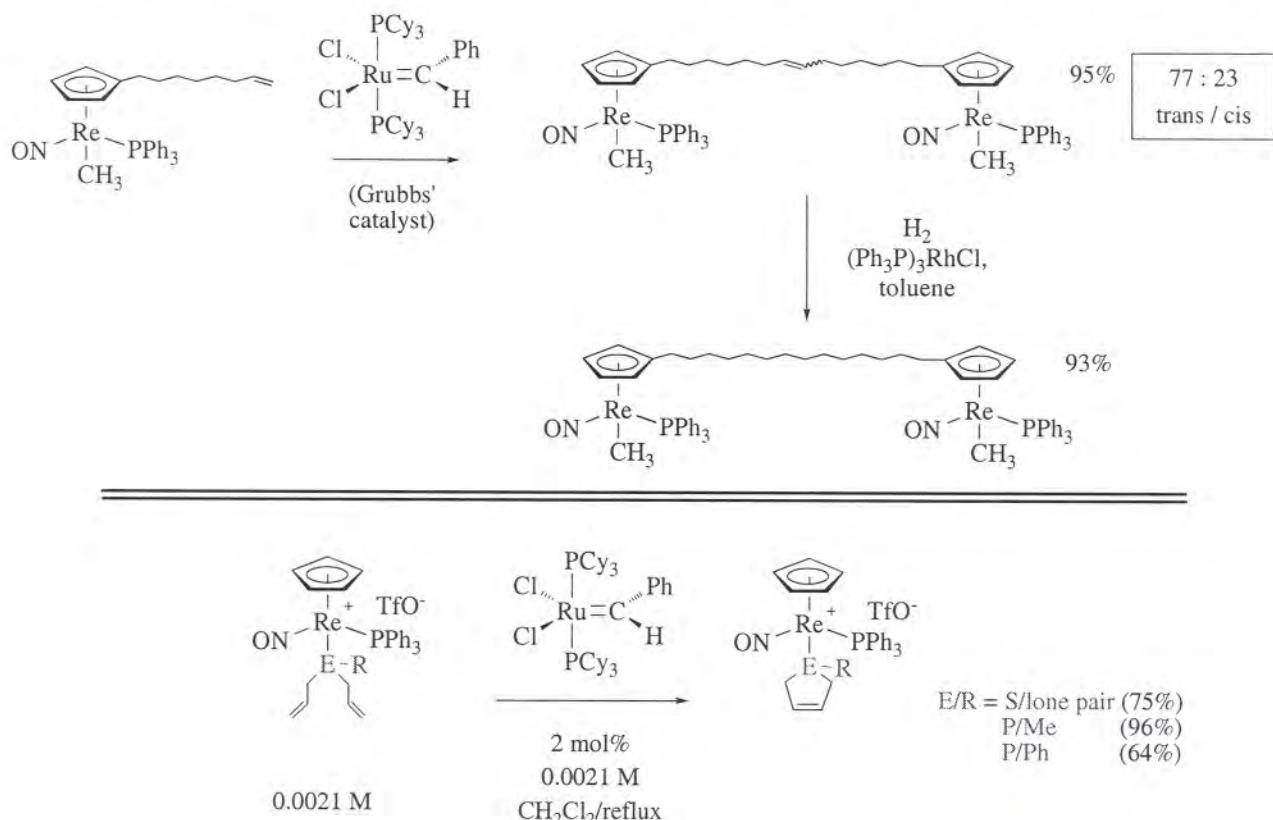
### C: Cyclization Between Two cis Ligands



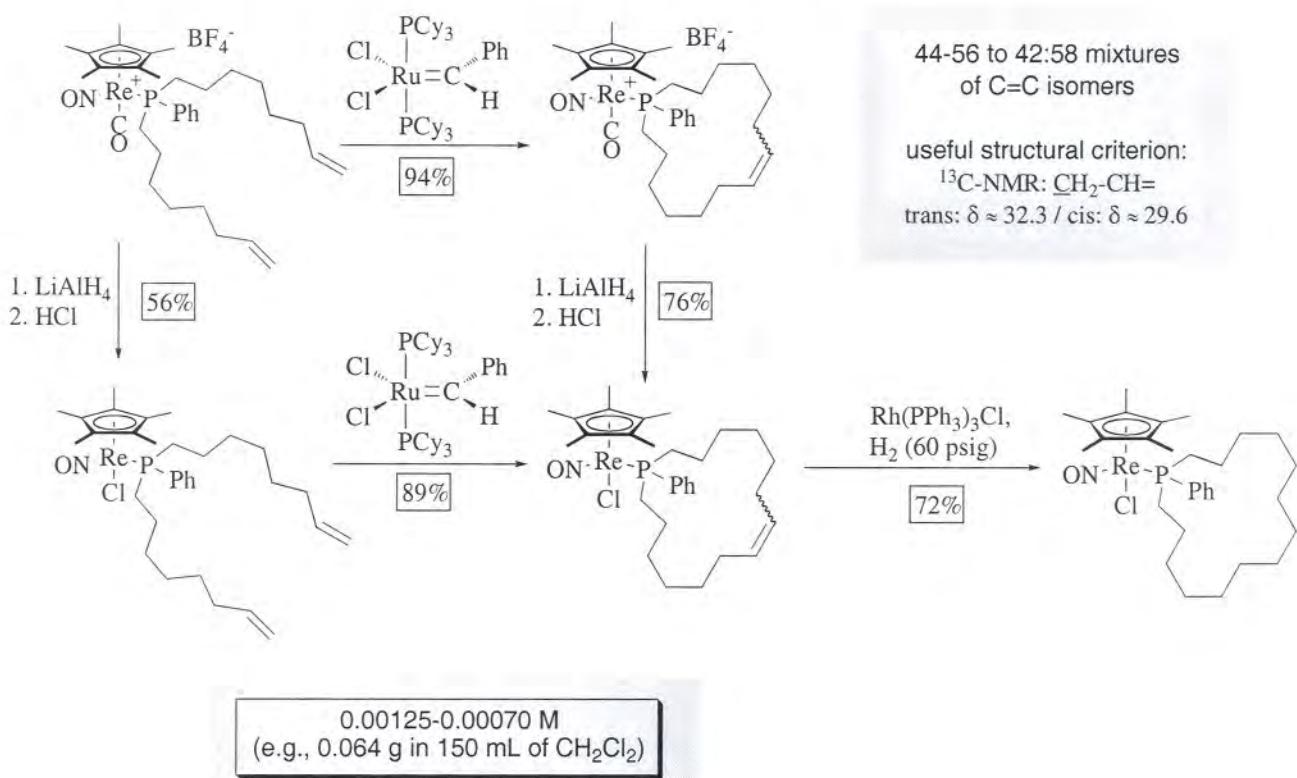
*review: OLEFIN METATHESIS IN METAL COORDINATION SPHERES*

Bauer, E.; Gladysz, J. A. in  
"Handbook of Metathesis" (R. H. Grubbs, Ed.) VCH (2003), Vol 2, 395-423

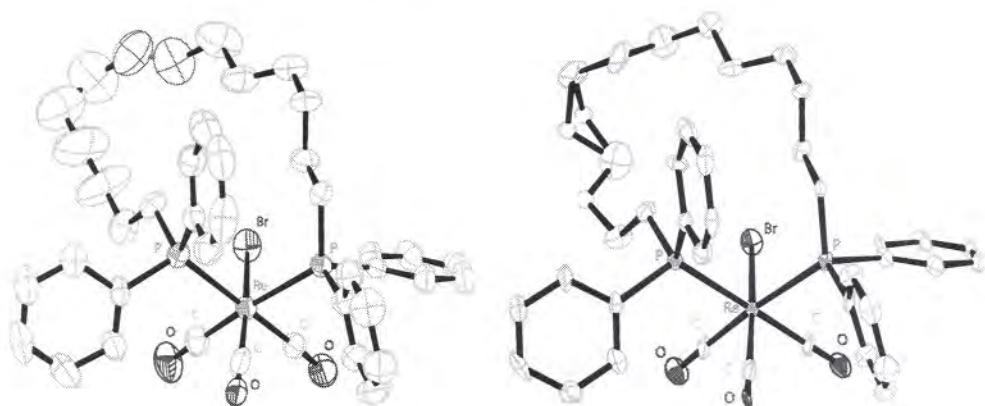
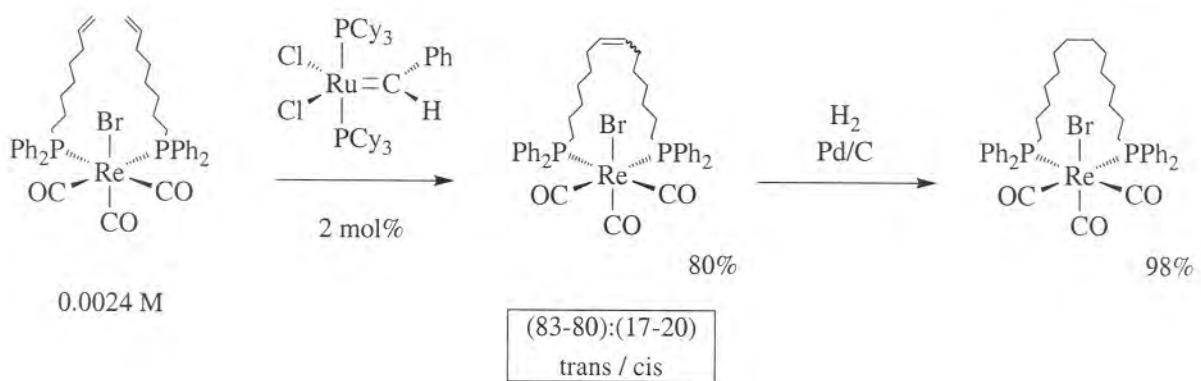
## JOINING TWO COMPLEXES; CYCLIZATION WITHIN A LIGAND



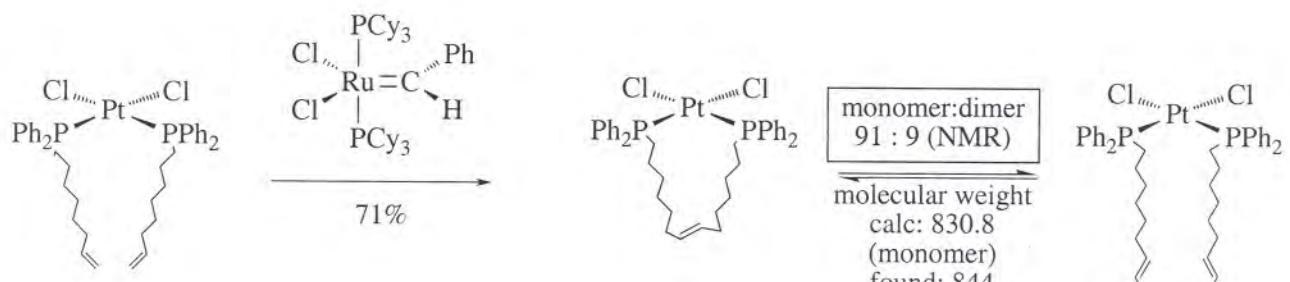
## CYCLIZATION WITHIN ONE LIGAND - LARGE RINGS



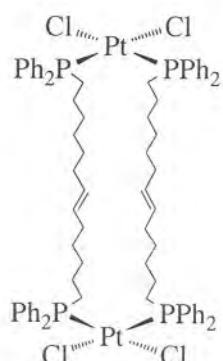
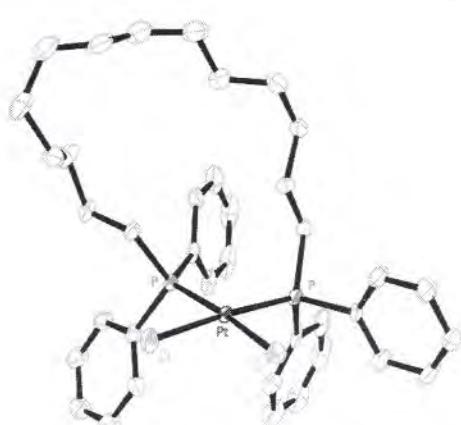
## CYCLIZATION BETWEEN TWO *cis*-LIGANDS



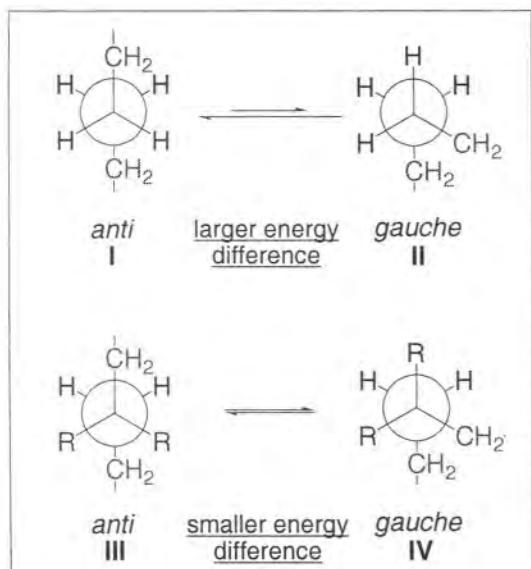
## CYCLIZATION WITHIN TWO *cis*-LIGANDS; SQUARE PLANAR PLATINAMACROCYCLES



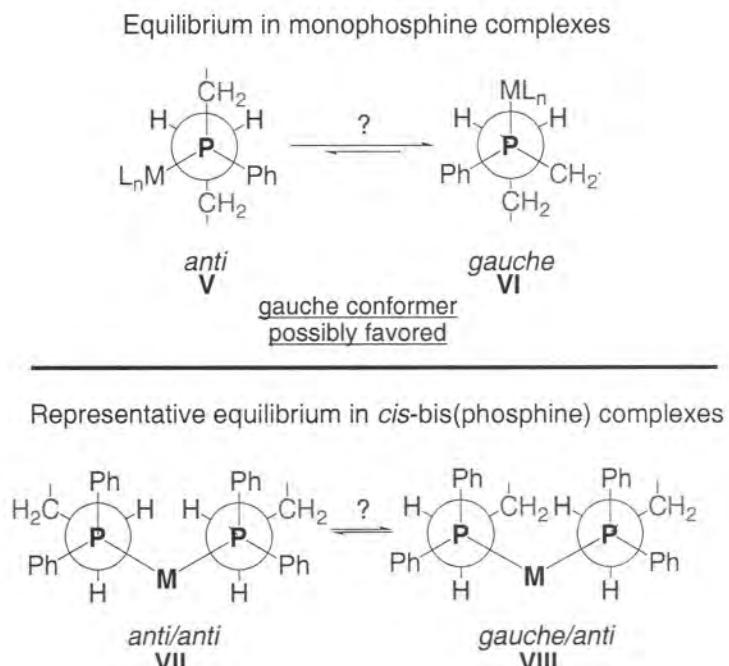
*similar data for  
thioether complexes*



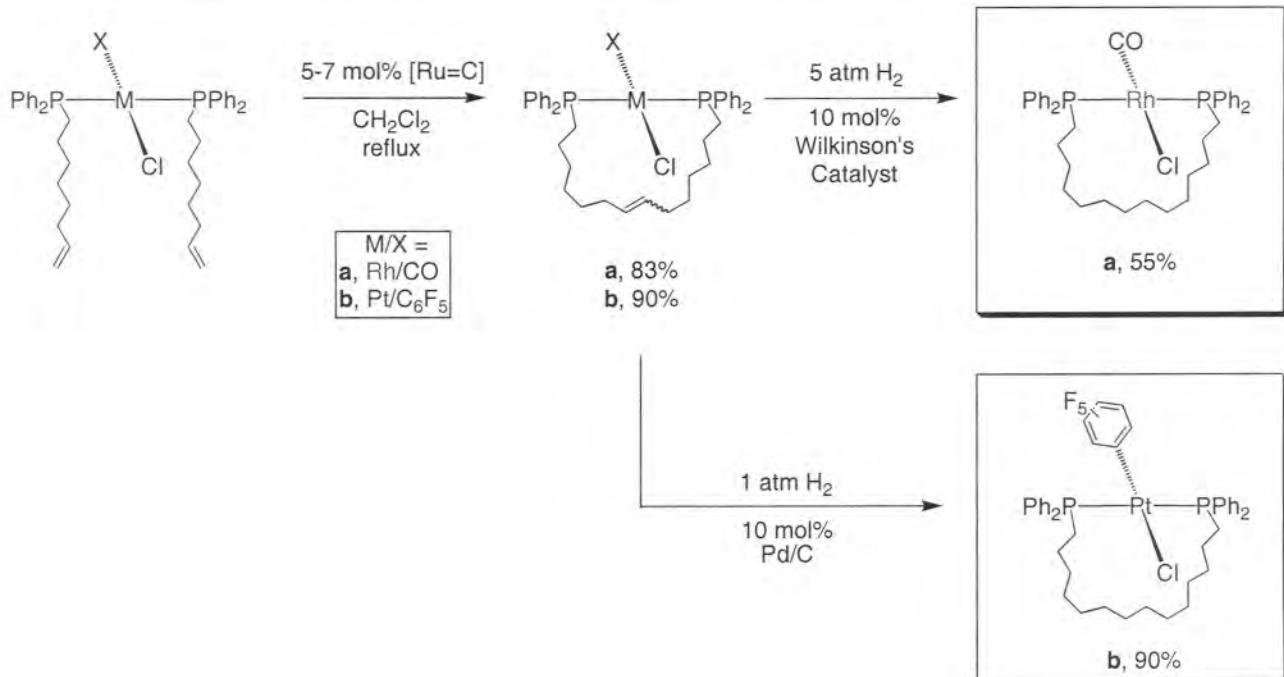
## MACROCYCLIZATIONS: KEY CONFORMATIONS and POSSIBLE "DRIVING FORCE"



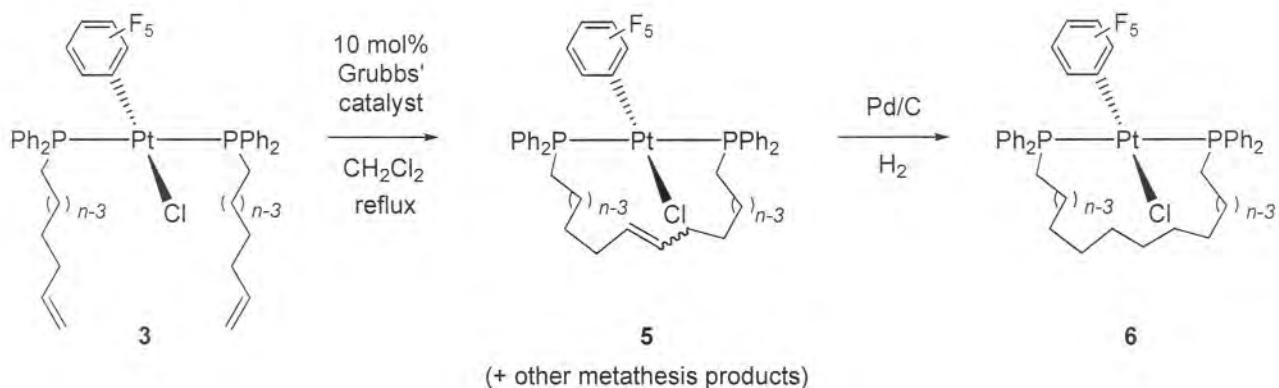
Germinal Dialkyl Effect  
or  
Thorpe-Ingold Effect



## CYCLIZATION BETWEEN TWO *trans*-LIGANDS



# EFFECT OF MACROCYCLE RING SIZE



$n = 4, \mathbf{a}, 95\%$

$6, \mathbf{b}, 96\%$

$8, \mathbf{c}, 90\%$

$9, \mathbf{d}, 85\%$

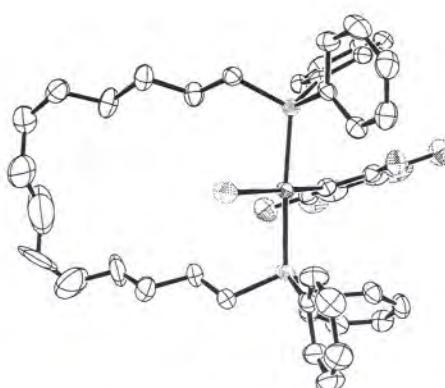
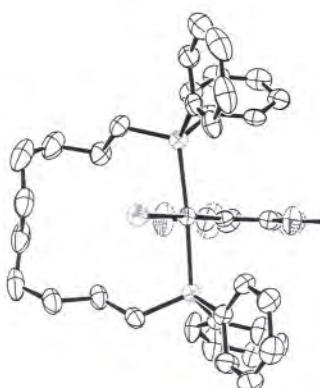
$n = 4, \mathbf{a}, 70\%$

$6, \mathbf{b}, 72\%$

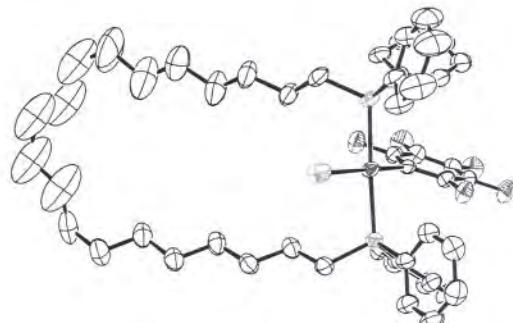
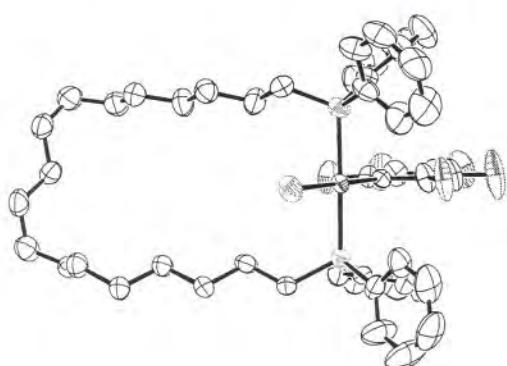
$8, \mathbf{c}, 59\%$

$9, \mathbf{d}, 50\%$

$n$	Number of $^{31}\text{P}$ NMR signals (crude)	Yield, major signal (crude, %)	Yield, all metathesis products (%)	Yield, major signal (purified, %)	Yield, all hydrogenation products (%)	Yield of <b>6</b> after purification (%)
4	5	84	95	80	87	70
6	2	87	96	88	94	72
8	5	67	90	67	86	59
9	5	48	85	54	76	50

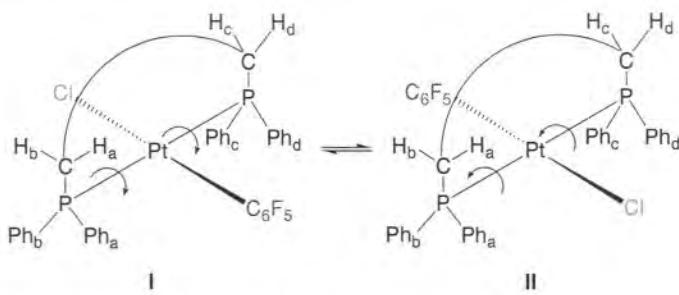


all Pt-P-C-C conformations gauche; all P-C-C-C conformations anti



five, three, five, and four C-C-C-C gauche segments

# EXCHANGE OF DIASTEREOTOPIC GROUPS REQUIRES ROTATION of MACROCYCLE over a Pt-XLIGAND



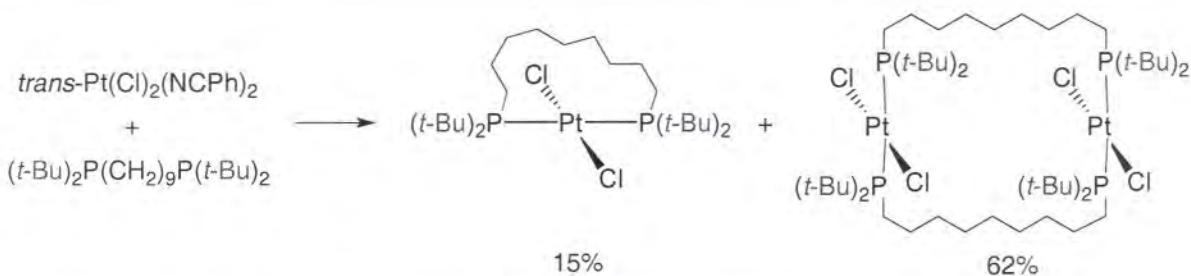
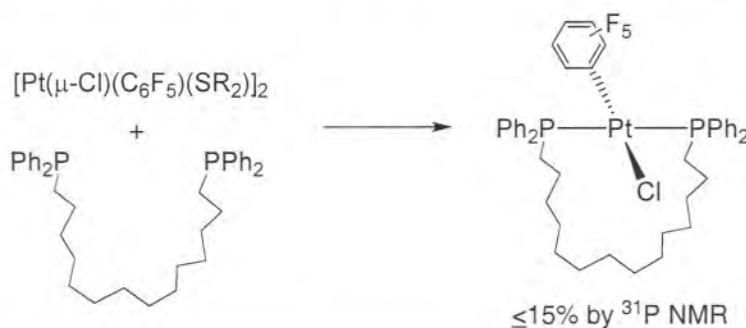
*enantiotopic:*  $H_a$  and  $H_d$ ;  $H_b$  and  $H_c$ ;  $Ph_a$  and  $Ph_d$ ;  $Ph_b$  and  $Ph_c$   
*diastereotopic:*  $H_a$  with  $H_b$  and  $H_c$ ;  $H_b$  with  $H_a$  and  $H_d$ ;  $H_c$  with  $H_a$  and  $H_d$ ;  $H_d$  with  $H_a$  and  $H_c$ ; phenyl groups analogous

the rotation  $I \rightarrow II$  exchanges diastereotopic groups  $H_b$  and  $H_d$ , and  $H_a$  and  $H_c$ , and analogous phenyl groups

10 methylene groups (13-membered ring):  $\Delta G^\ddagger > 17.4$  kcal/mol (95 °C)  
 14 methylene groups (17-membered ring):  $\Delta G^\ddagger < 8.4$  kcal/mol (-90 °C)

distance from platinum to remote carbon of macrocycle: 5.62 Å and 7.83 Å  
 subtract van der Waals radius of carbon: 3.92 Å and 6.13 Å  
 platinum-carbon bond length: 2.36 Å  
 add van der Waals radius of chlorine: 4.14 Å

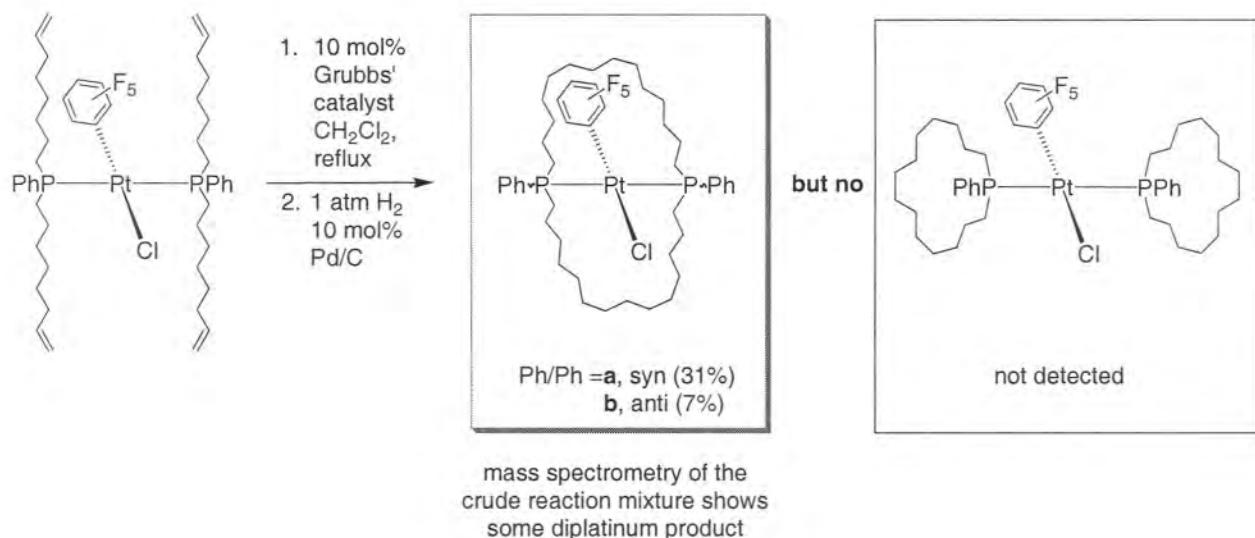
## CONTROL EXPERIMENTS and LITERATURE PRECEDENT



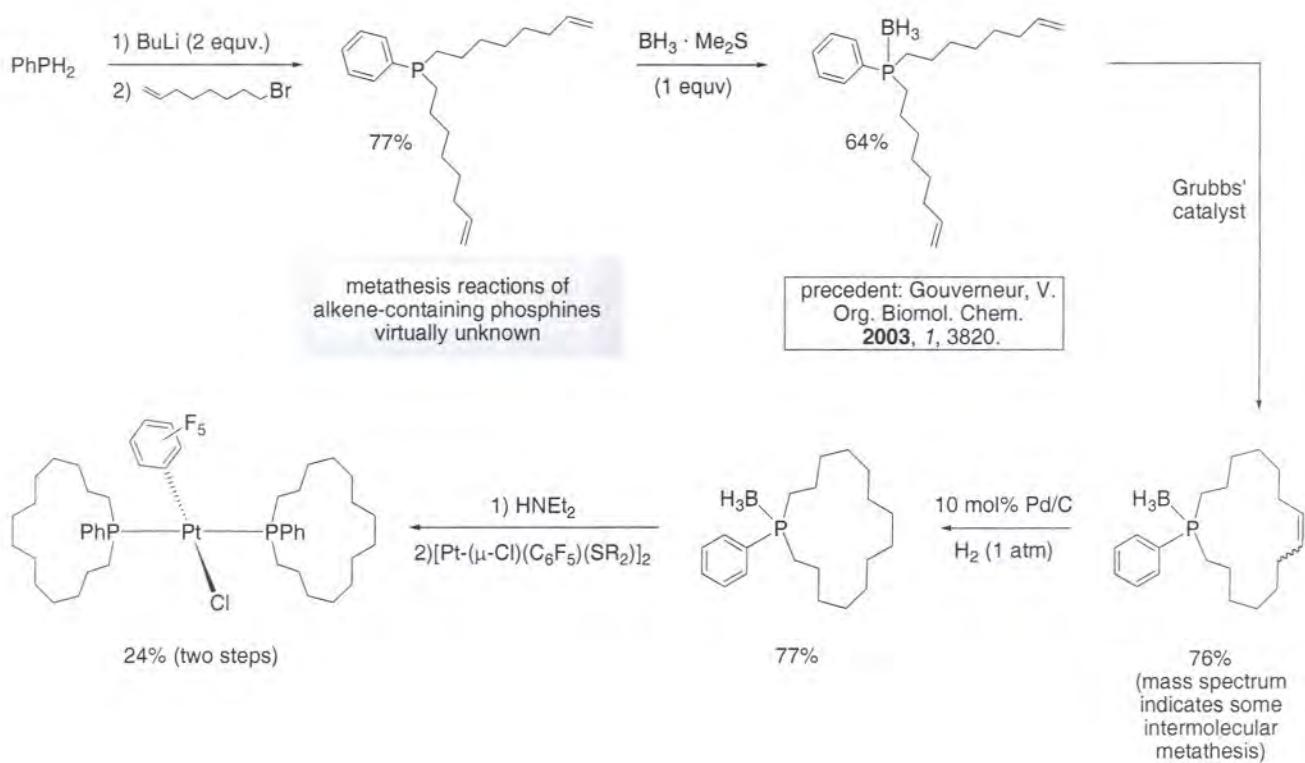
analogous  $PPh_2$  compound gives only oligomer (also with  $(CH_2)_{10}$  or  $(CH_2)_{12}$  bridges)

shortest known trans-spanning ligand (nine methylene groups, twelve-membered ring)  
 Shaw, J. Am. Chem. Soc. 1975  
 and J. Chem. Soc. Dalton 1976

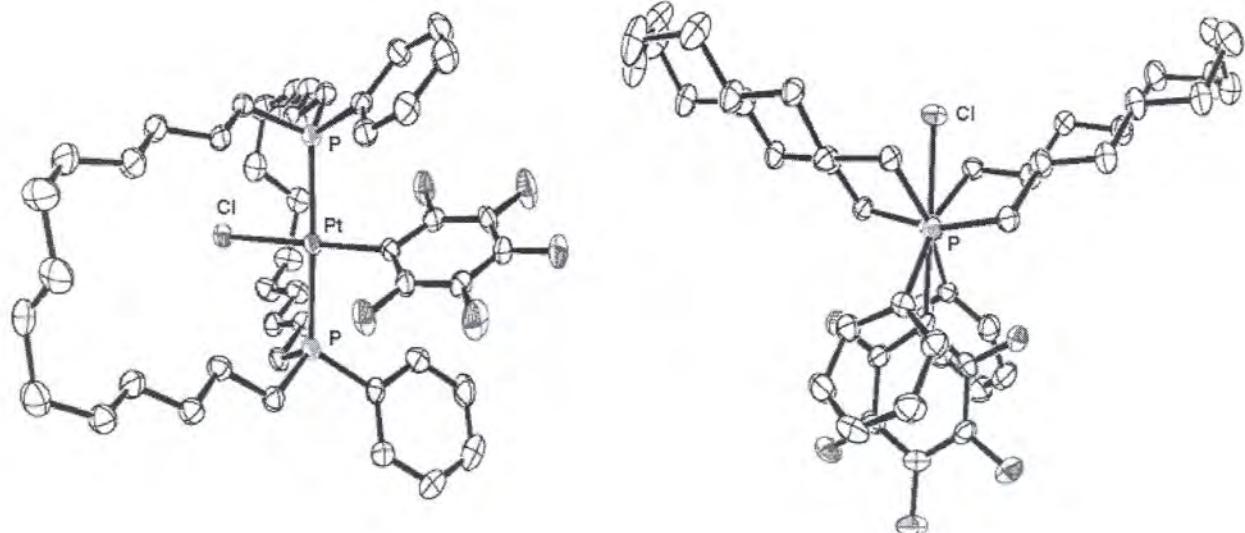
# CYCLIZATION BETWEEN TWO trans-LIGANDS, Each With Two Alkenes



## INDEPENDENT SYNTHESIS of ALTERNATIVE MACROCYCLIZATION PRODUCT

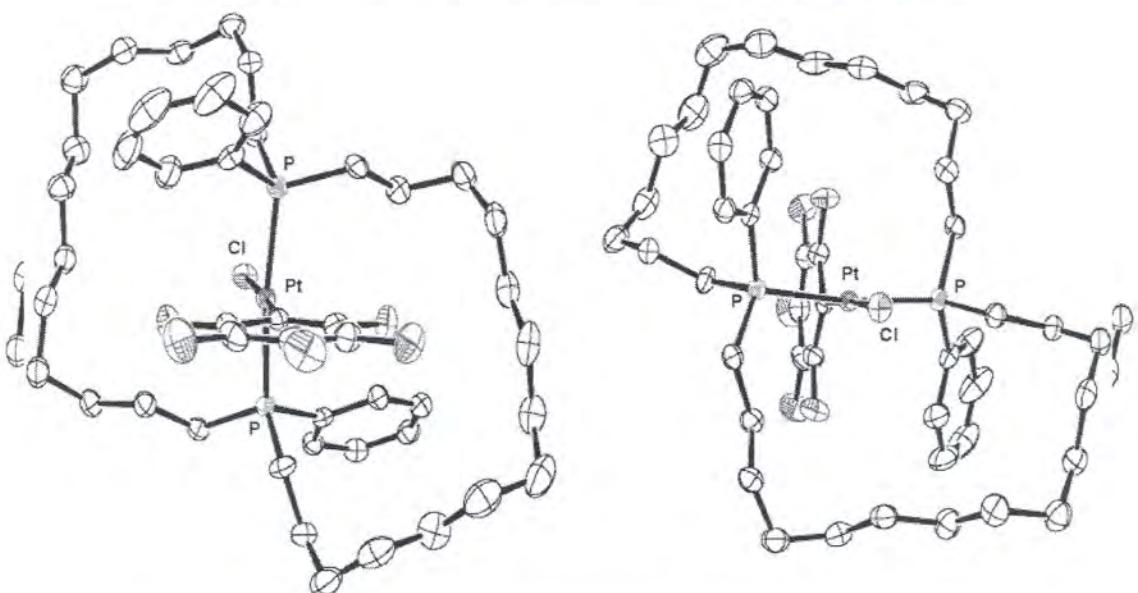


## CRYSTAL STRUCTURE OF SYN ISOMER



molecule has idealized  $C_{2v}$  symmetry  
(homotopic PPh groups; seven  $\text{CH}_2$   $^{13}\text{C}$  NMR signals)  
macrocycle conformation similar to mono-bridged species

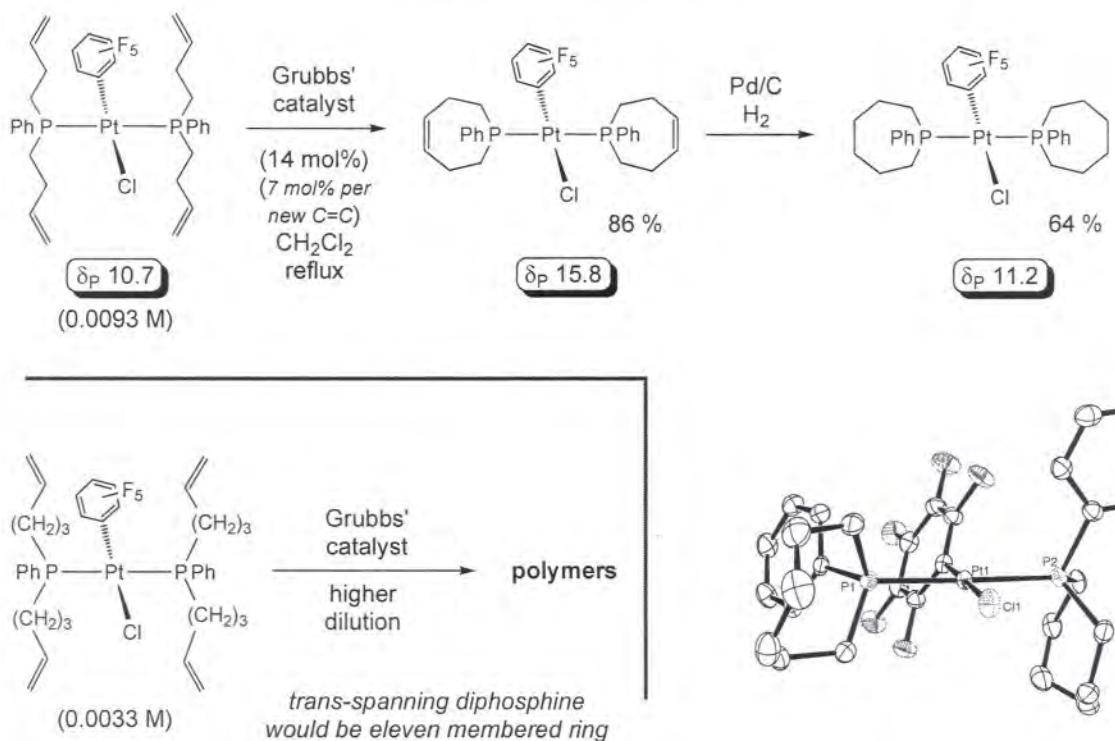
## CRYSTAL STRUCTURE OF ANTI ISOMER



molecule has idealized  $C_1$  symmetry  
(diastereotopic PPh groups with distinct NMR signals;  
up to 28  $\text{CH}_2$   $^{13}\text{C}$  NMR signals)  
macrocycle conformation very different from syn isomer  
(one anti Pt-P-C-C segment, six gauche C-C-C-C segments)

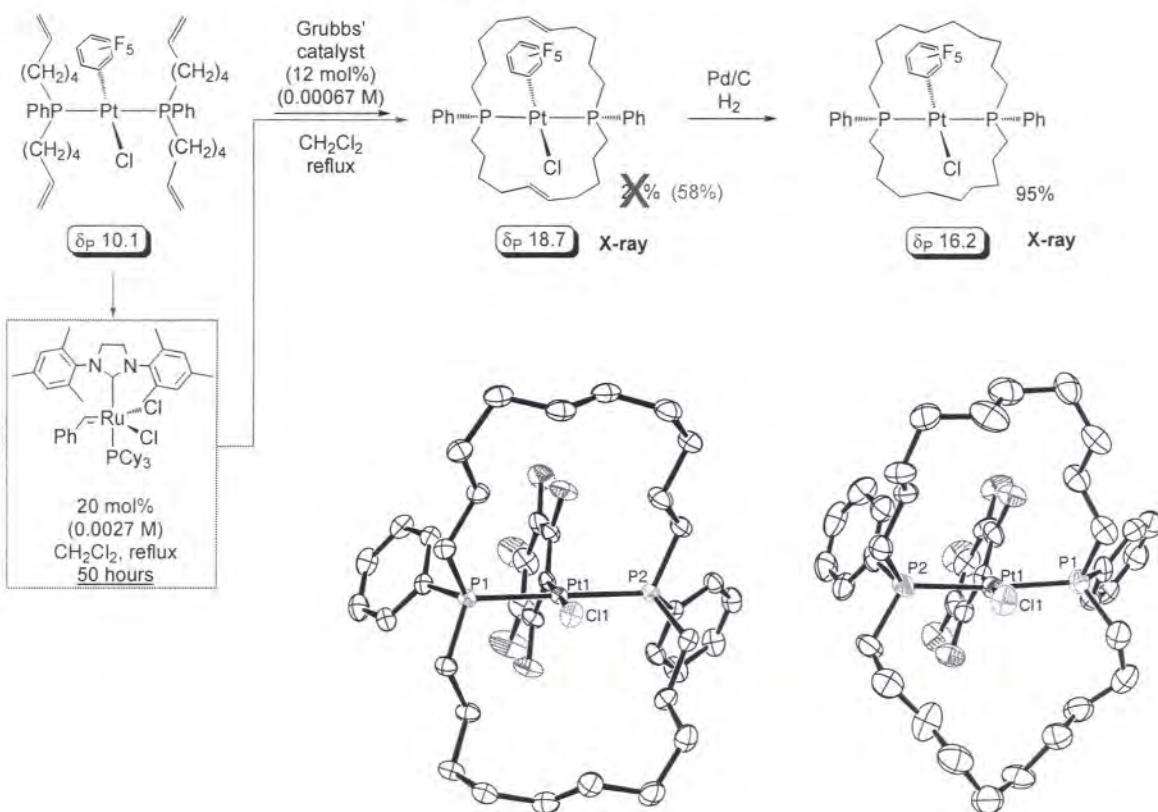
# OTHER DICYCLIZATION REACTIONS

*two and three methylene groups*

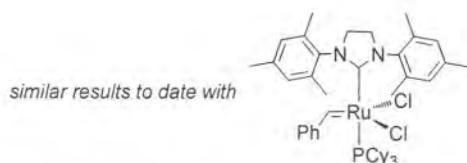
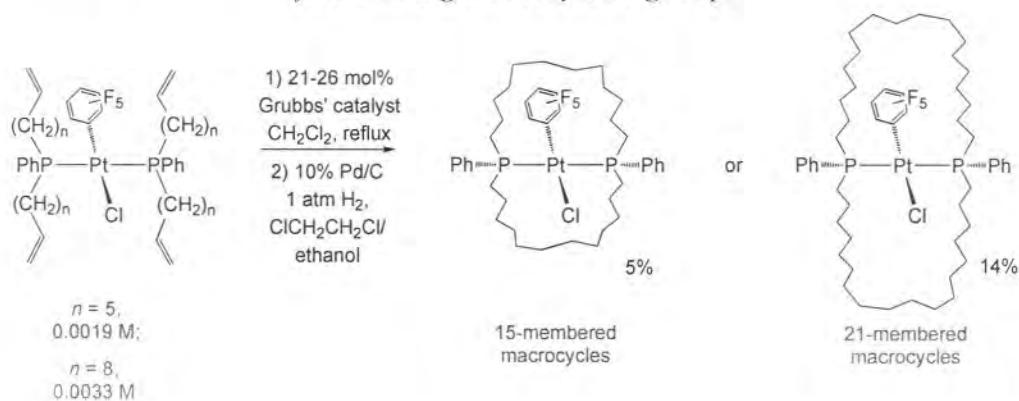


## DIMACROCYCLIZATION TO DOUBLY TRANS-SPANNING DIPHOSPHINE

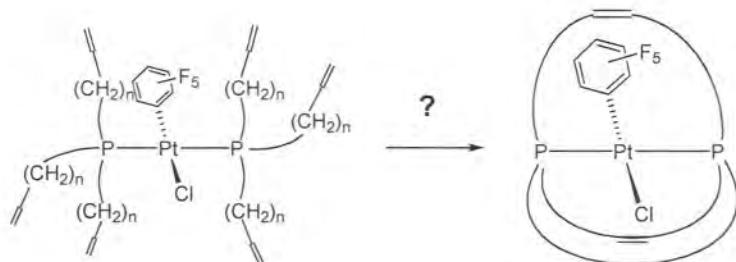
*four methylene groups*



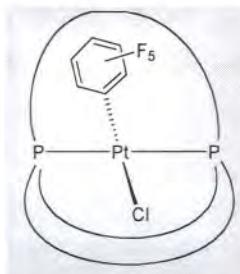
DIMACROCYCLIZATION TO DOUBLY TRANS-SPANNING DIPHOSPHINE  
*five and eight methylene groups*



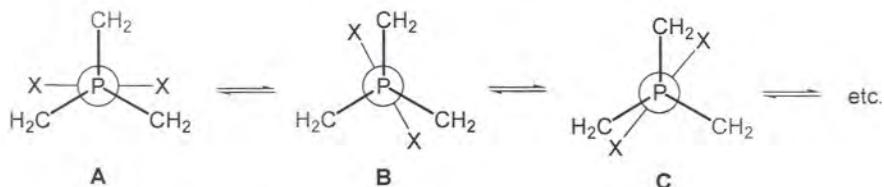
NEXT GENERATION TARGET: A "MOLECULAR GYROSCOPE"



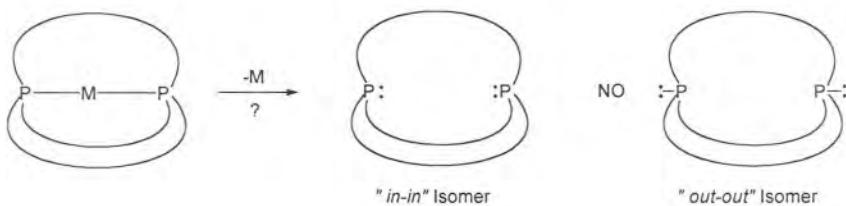
## SPECIAL FEATURES OF TARGET MOLECULES



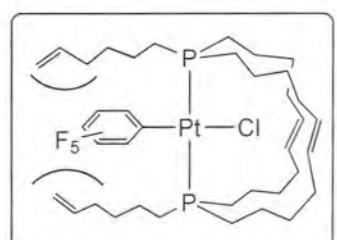
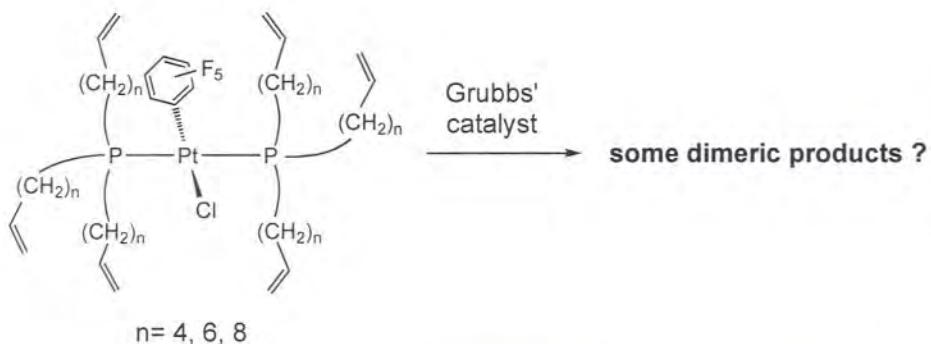
rate of rotation or "gyroscope spinning" can be probed by dynamic NMR



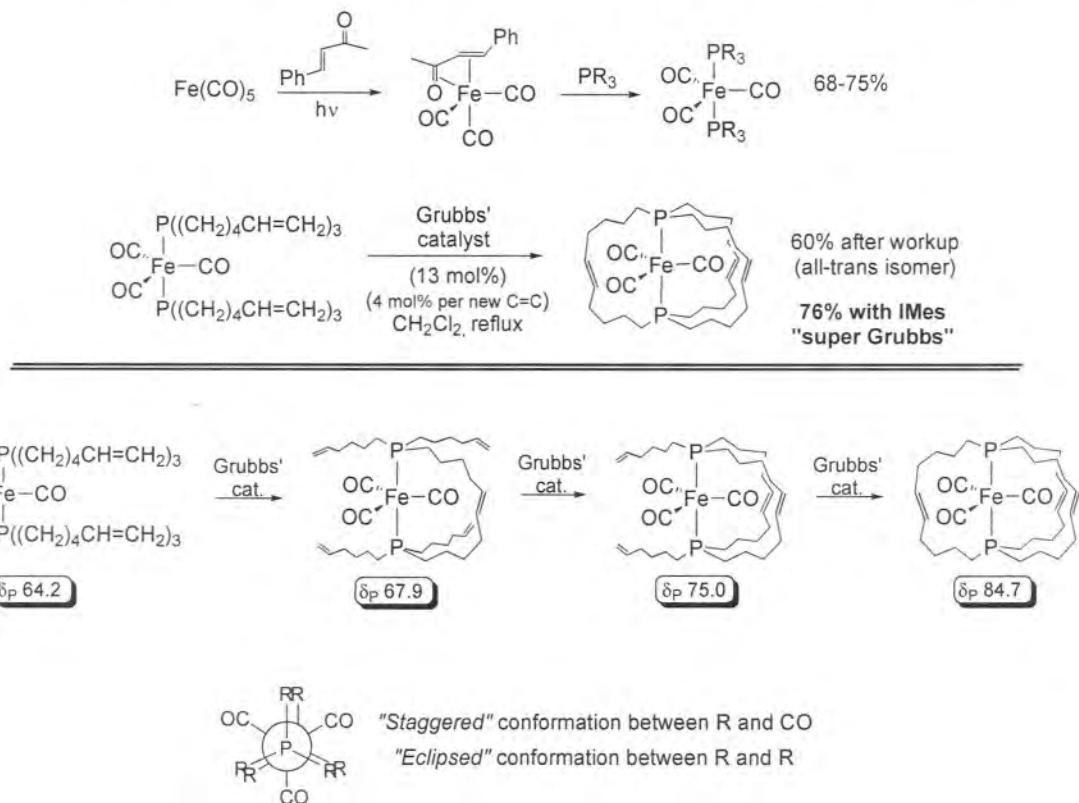
removal of metal would selectively give difficult-to-obtain in-in isomer of bridgehead diphosphine



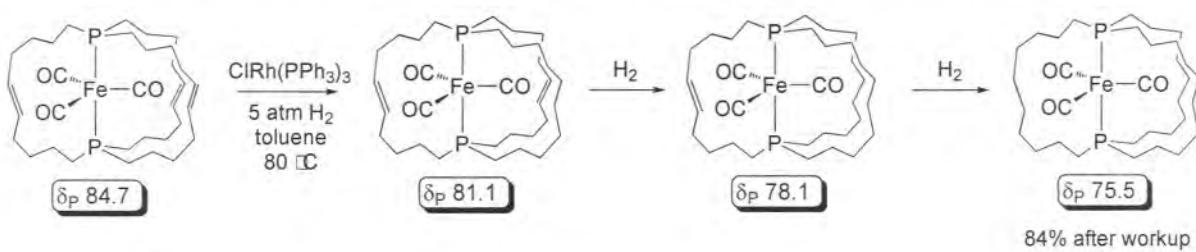
## INITIAL EXPERIMENTS ARE DISASTERS



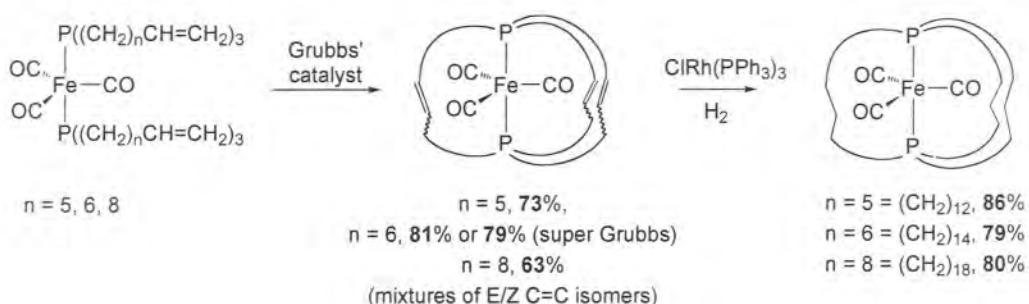
## SECOND GENERATION APPROACH TO ORGANOMETALLIC GYROSCOPES



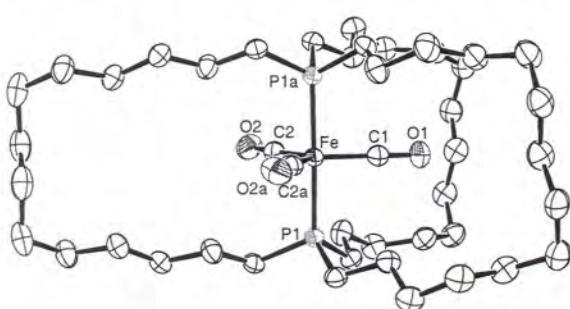
## HYDROGENATION PROCEEDS SMOOTHLY IN A STEPWISE MANNER



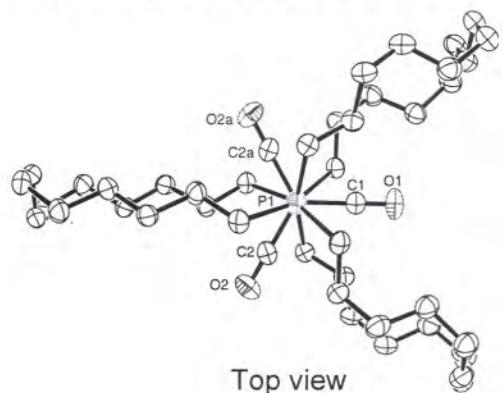
the methylene bridge length may be increased:



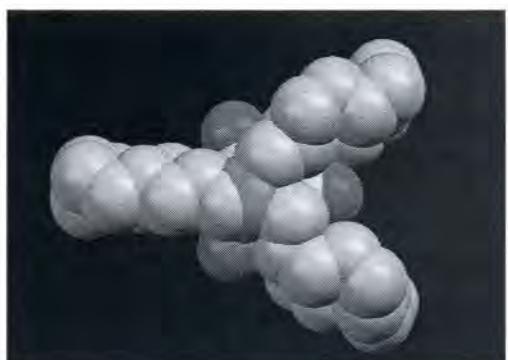
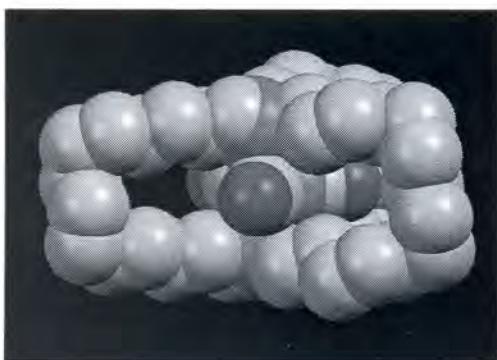
# FIRST CRYSTAL STRUCTURE OF GYROSCOPE-TYPE COMPLEX



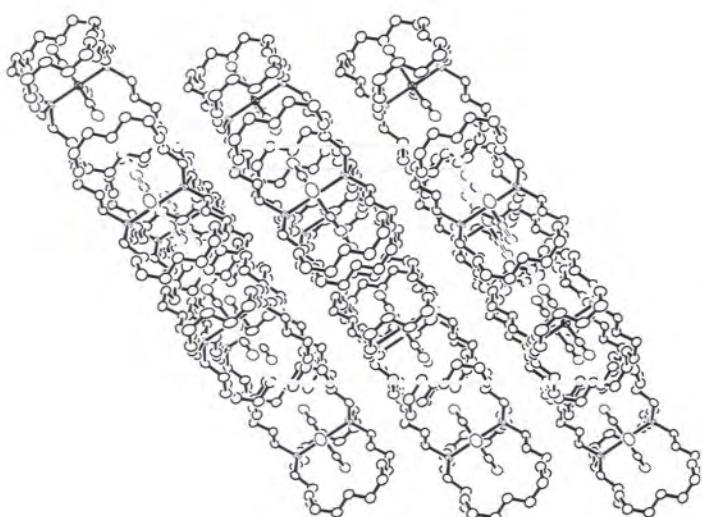
Side view



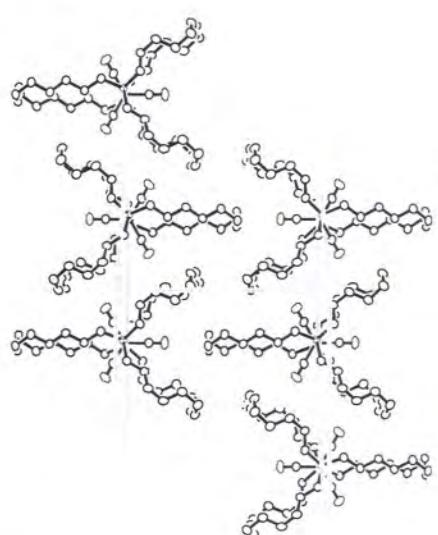
Top view



crystal packing of gyroscope type complex  
(rotator axes are aligned)

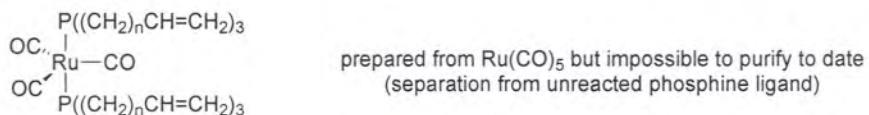
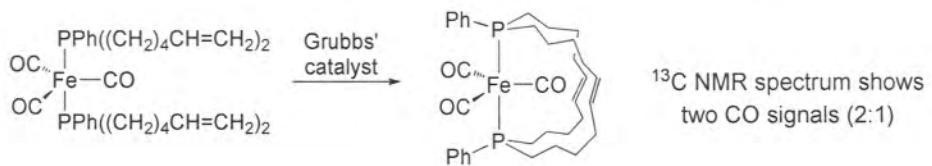


View from *b* axis

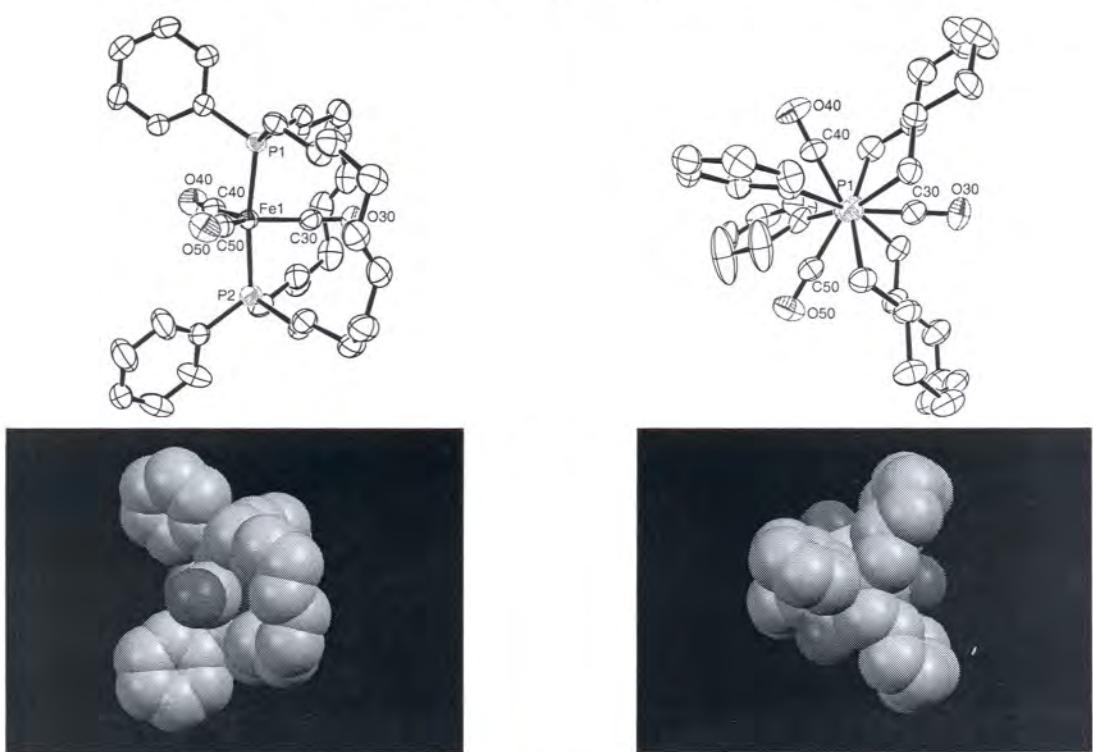


View from *a* axis

## RELATED MACROCYCLIZATIONS



### Crystal Structure of Doubly-Bridged Complex



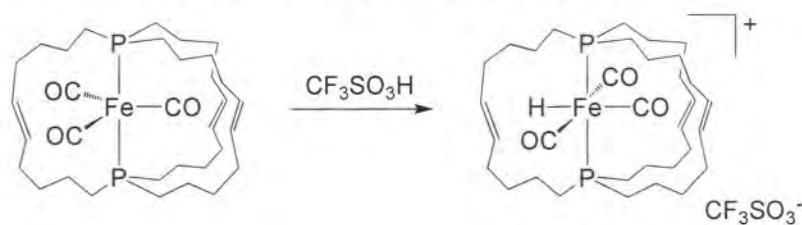
Distance from iron to remote carbon of macrocycles: 5.40 and 5.54 Å

Subtract van der Waals radius of carbon: 3.84 and 3.71 Å

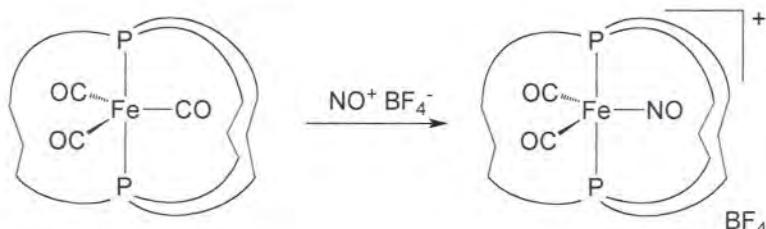
Fe-C-O bond length: 2.93 Å

Add van der Waals radius of oxygen: 4.45 Å

## REACTIONS OF GYROSCOPE MOLECULES



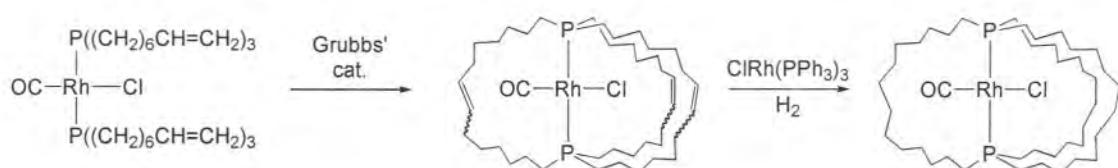
NMR spectra:  
two sets of  $\text{CH}=\text{CH}$   
protons and carbons  
(2:1, RT and 80  $^\circ\text{C}$ )



$n = 4$  (ten methylene groups)  
 $^{13}\text{C}$  NMR spectrum shows two bridges (2:1)  
 $n = 5$  (twelve methylene groups)  
 $^{13}\text{C}$  NMR spectrum shows two bridges (2:1)  
 $n = 6$  (fourteen methylene groups)  
 $^{13}\text{C}$  NMR spectrum shows one bridge

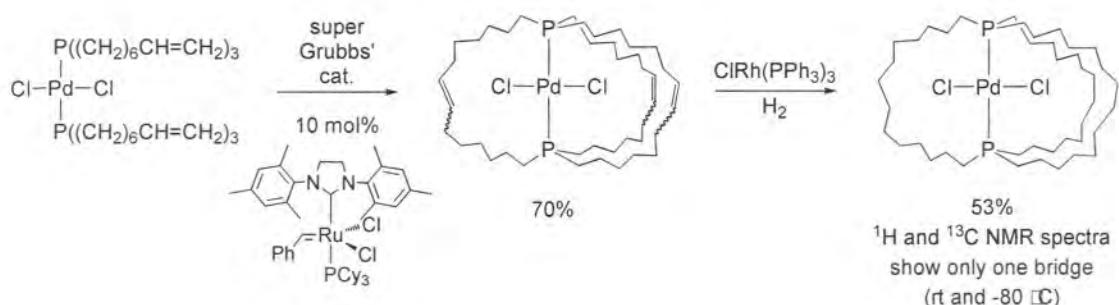
## THIRD GENERATION APPROACH TO ORGANOMETALLIC GYROSCOPES

square planar complexes with two small ligands

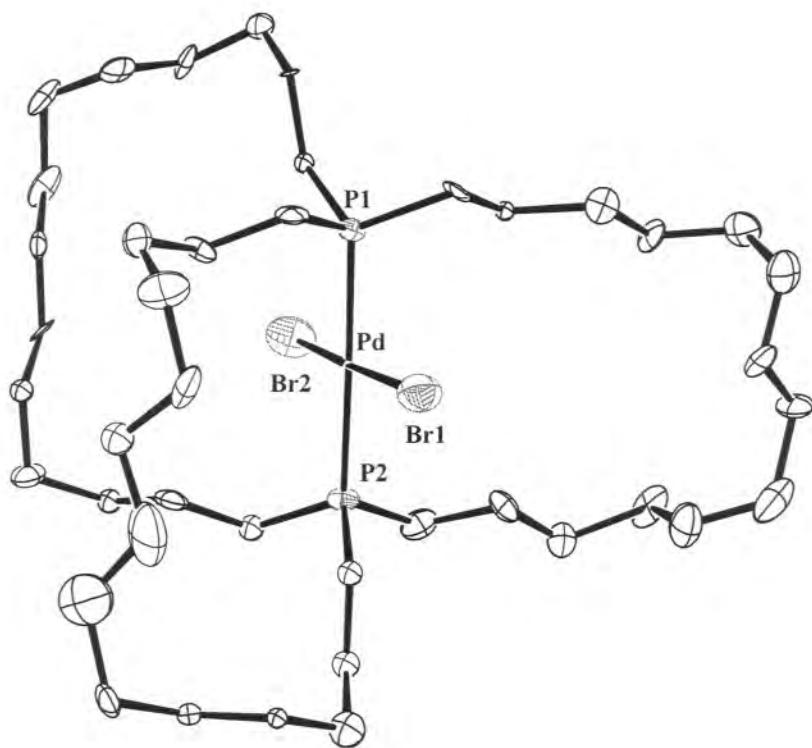


promising preliminary data with  $(\text{CH}_2)_4$  and iridium analogs

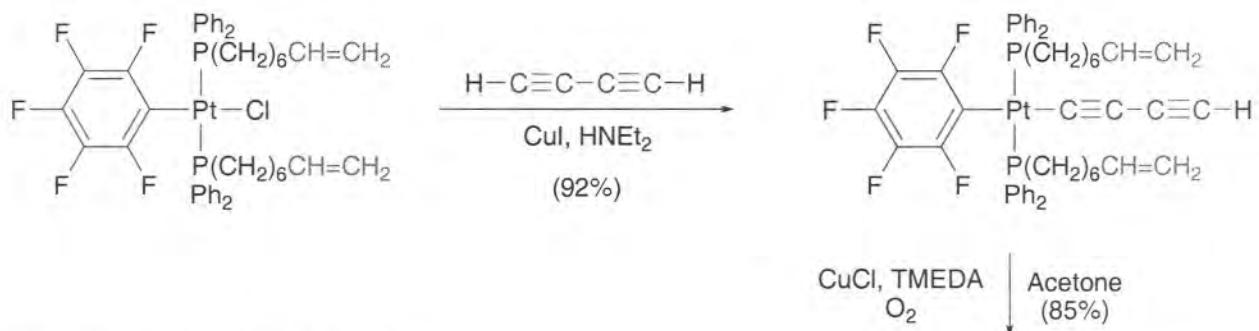
14% overall;  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra  
show only one bridge  
(rt and -80  $^\circ\text{C}$ )



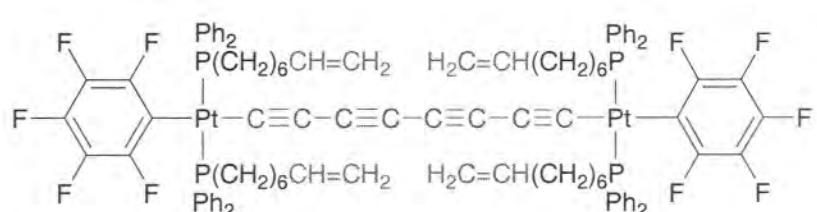
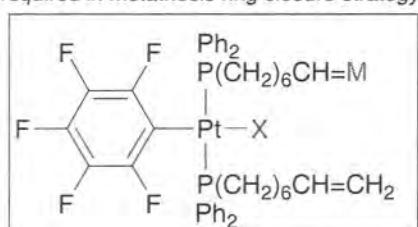
# CRYSTAL STRUCTURE of PdBr<sub>2</sub> GYROSCOPE



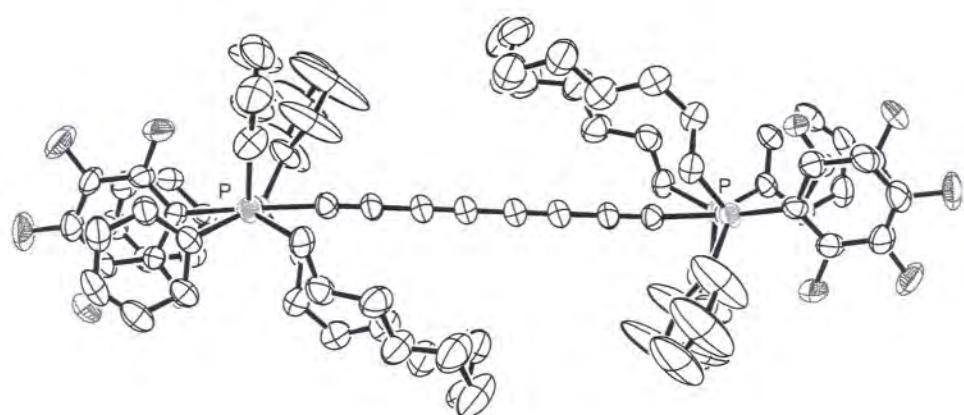
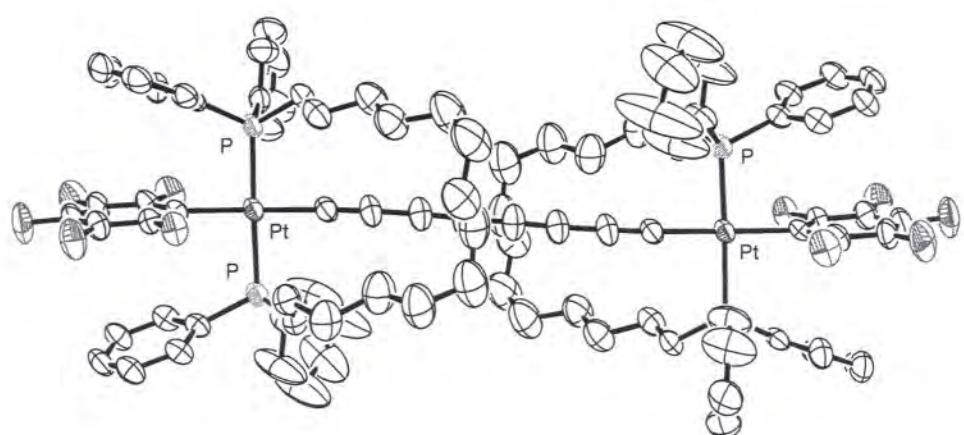
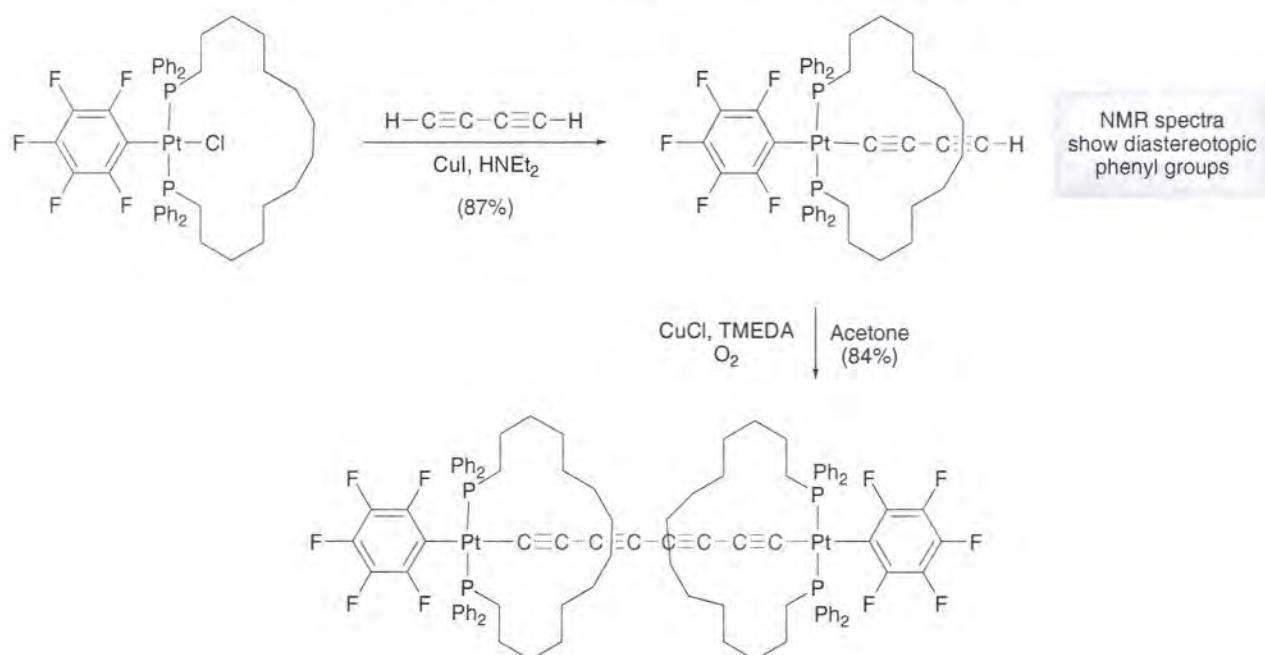
## TOWARDS OTHER ARCHITECTURALLY SOPHISTICATED TARGETS



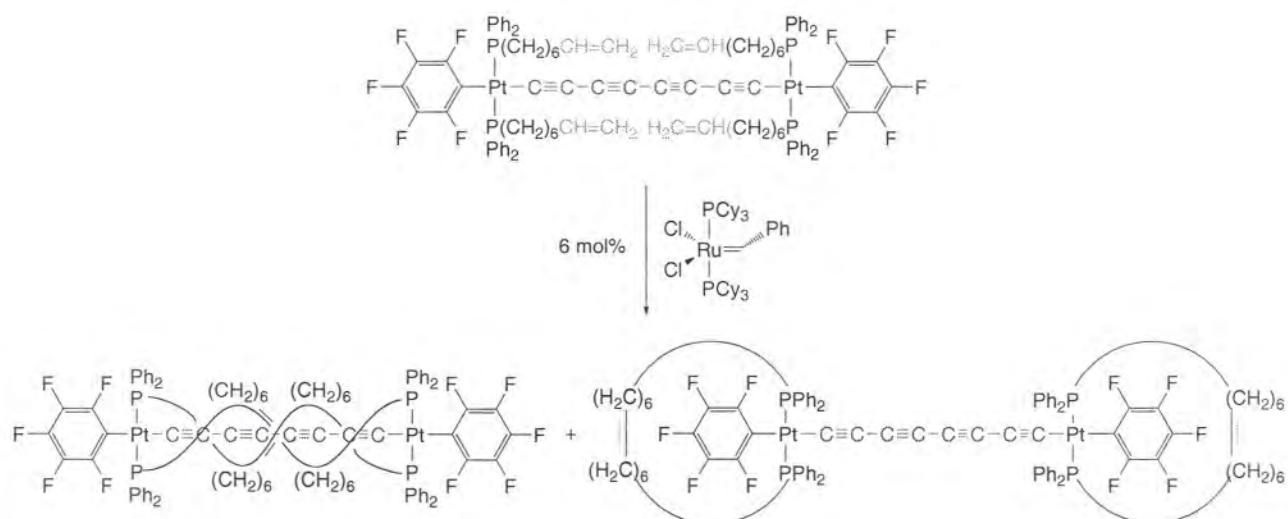
*required in metathesis ring closure strategy:*



CARBON CHAIN COMPLEXES FROM *trans*-SPANNING PHOSPHINE COMPLEX;  
synthesis of an authentic sample of a possible by-product

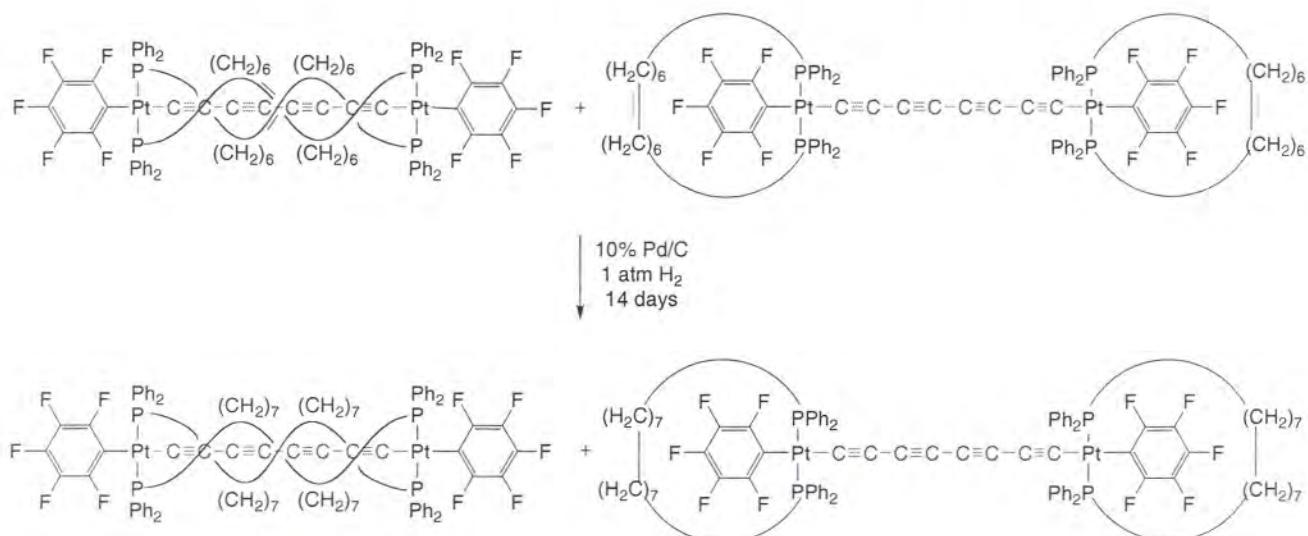


## METATHESIS of DIPLATINUM TETRAOLEFIN

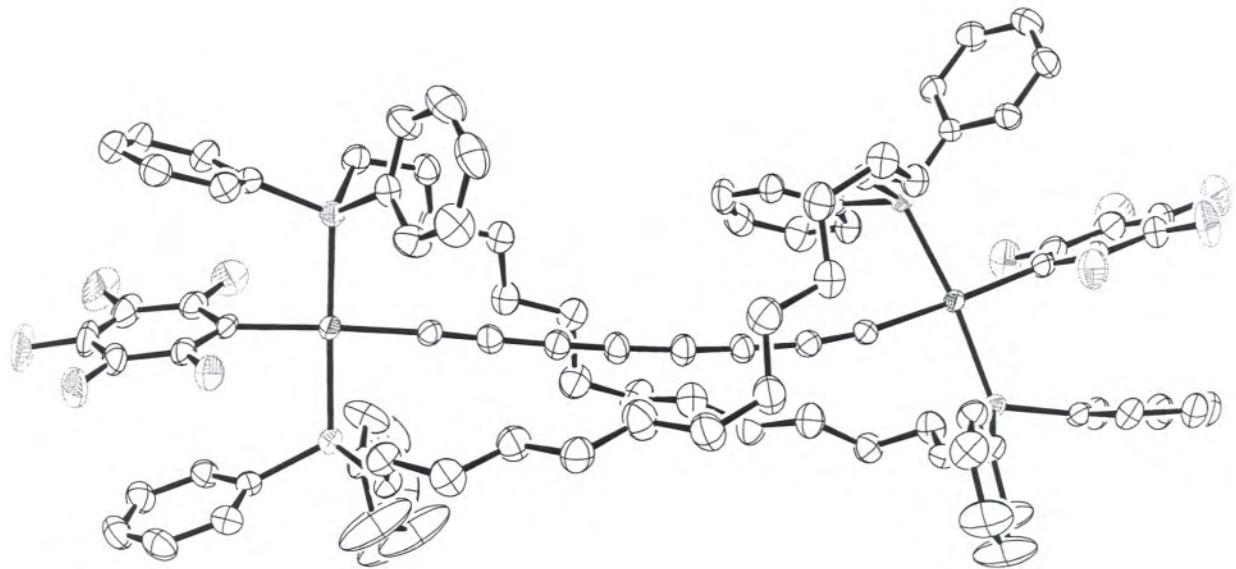


96% yield of "analytically pure" mixture  
 $^{31}\text{P}$  NMR shows five major peaks (64:11:8:9:8)

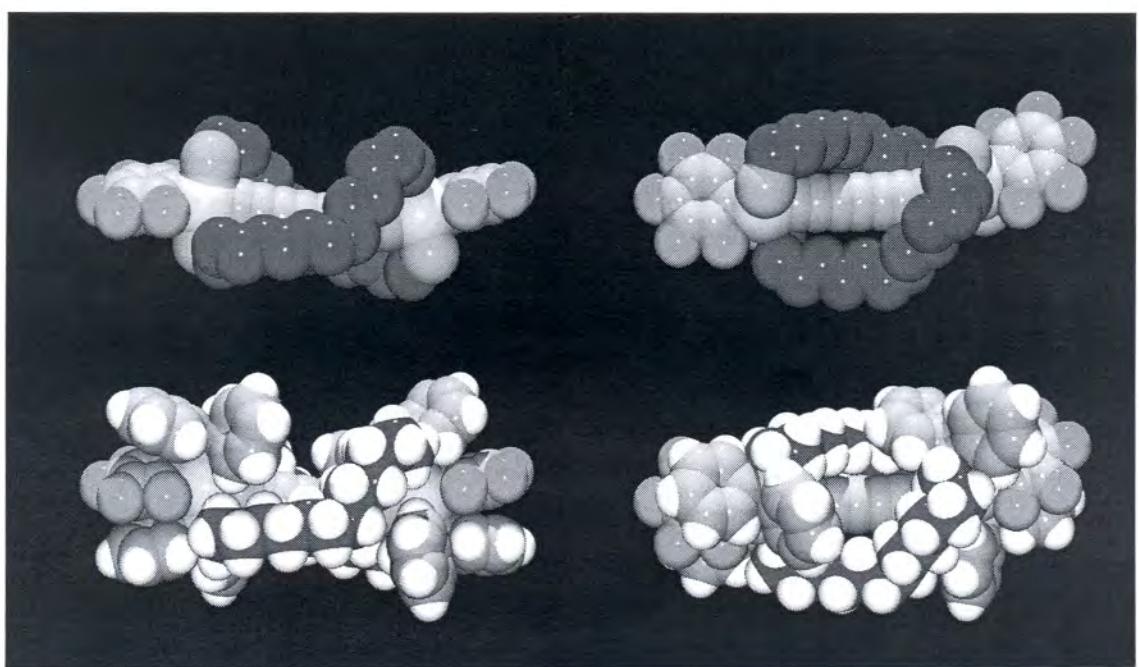
## FIRST SYNTHESIS OF TARGET MOLECULE



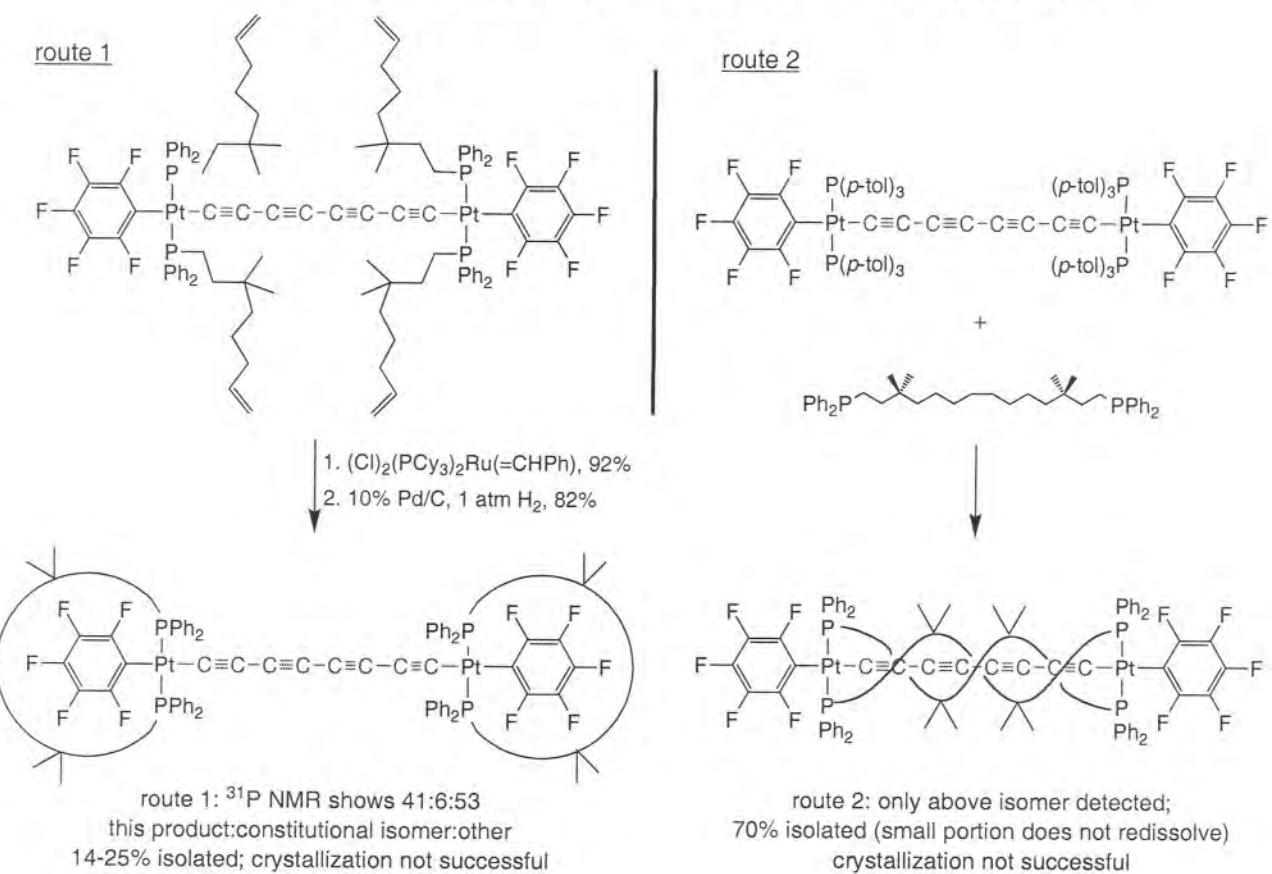
93% overall yield for two steps;  
 mass spectra show only expected molecular ion but  
 $^{31}\text{P}$  NMR spectra sometimes show more than two peaks;  
 preparative TLC gives the "protected chain" complex in 32% yield



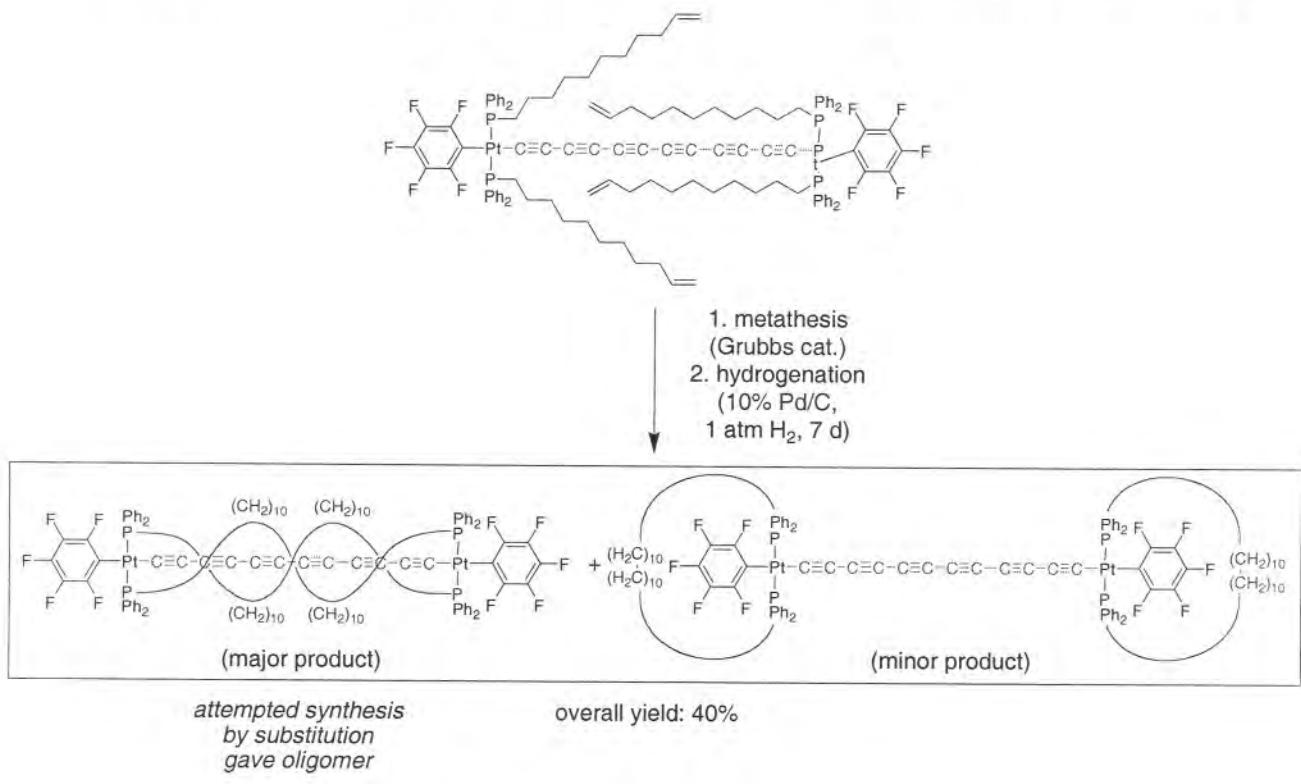
VIEWS OF THE PPh<sub>2</sub> BASED DOUBLE HELIX



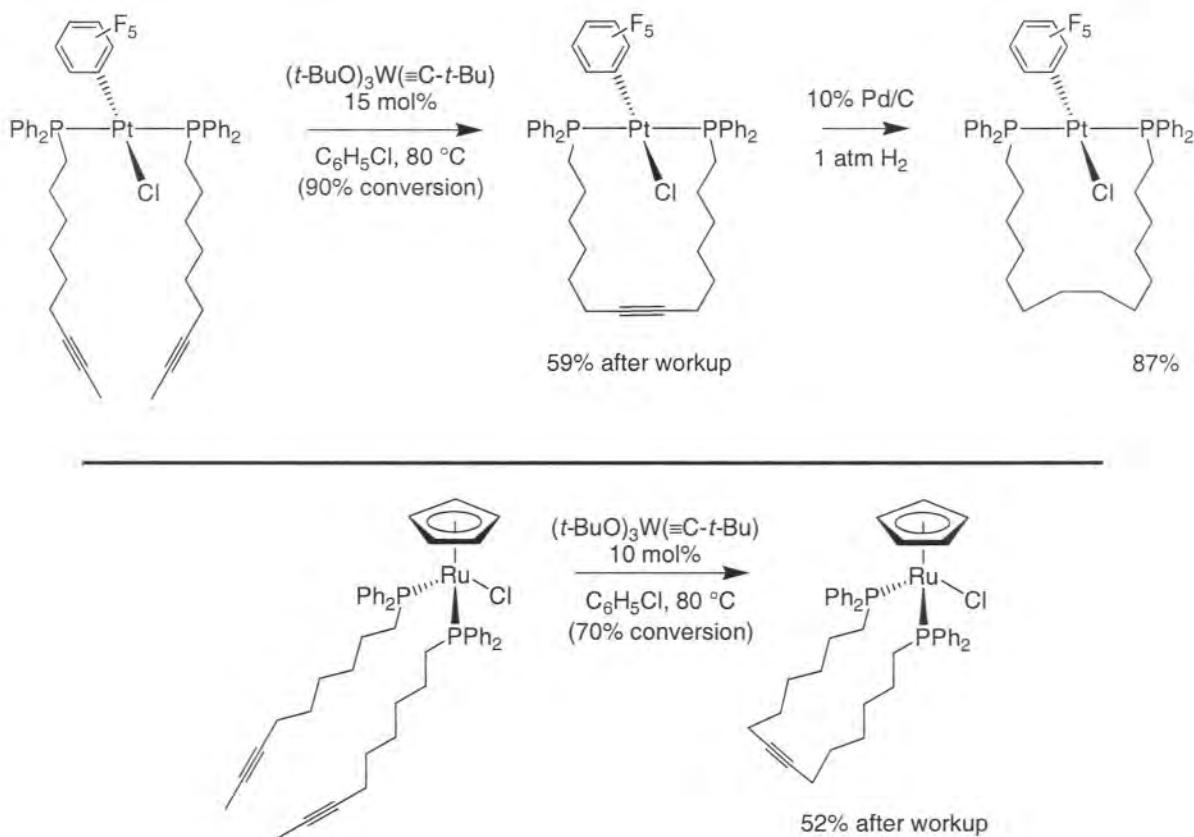
## INTRODUCTION of GEMINAL DIMETHYL GROUPS



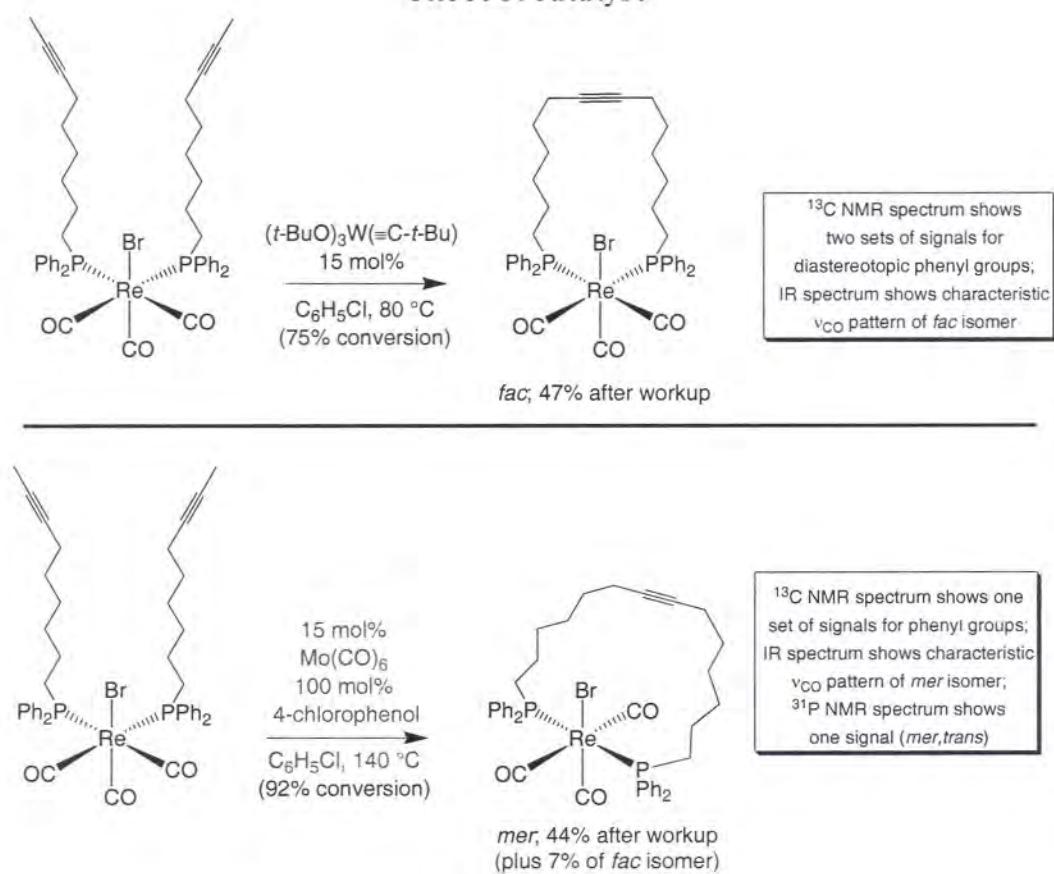
## PtC<sub>12</sub>Pt SERIES: OLEFIN METATHESIS APPROACH TO DOUBLE HELIX



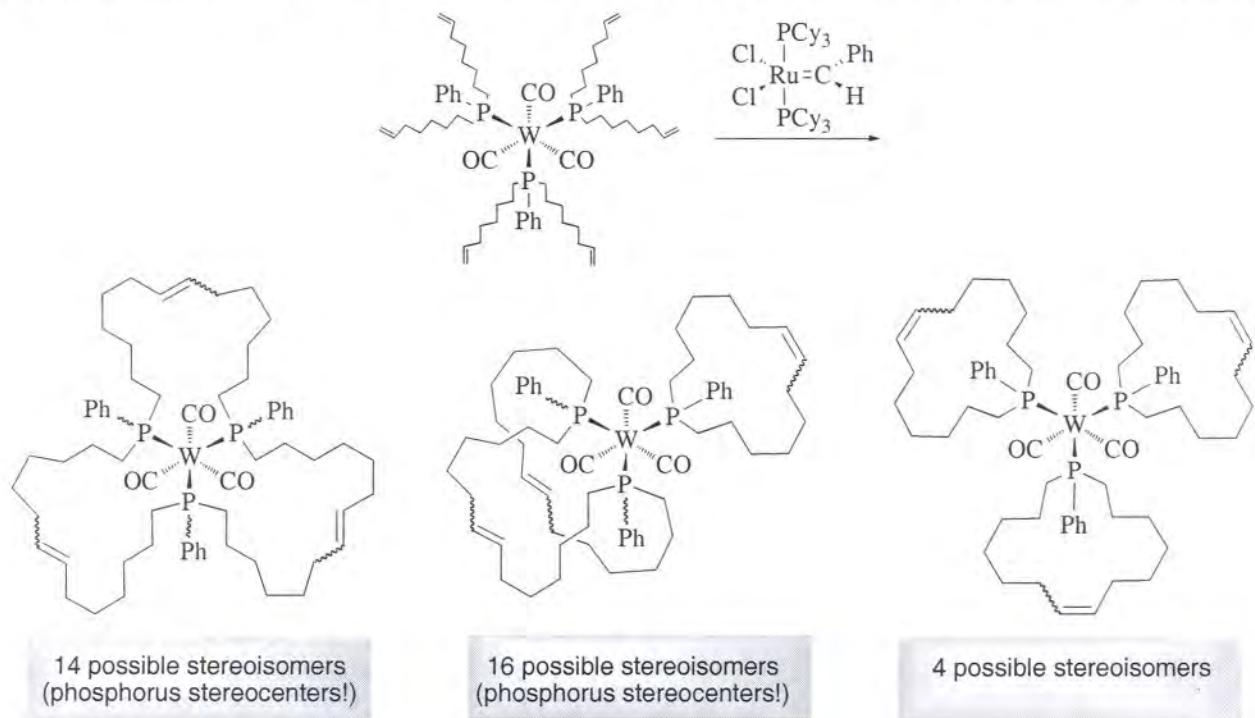
## ALKYNE METATHESIS in METAL COORDINATION SPHERES



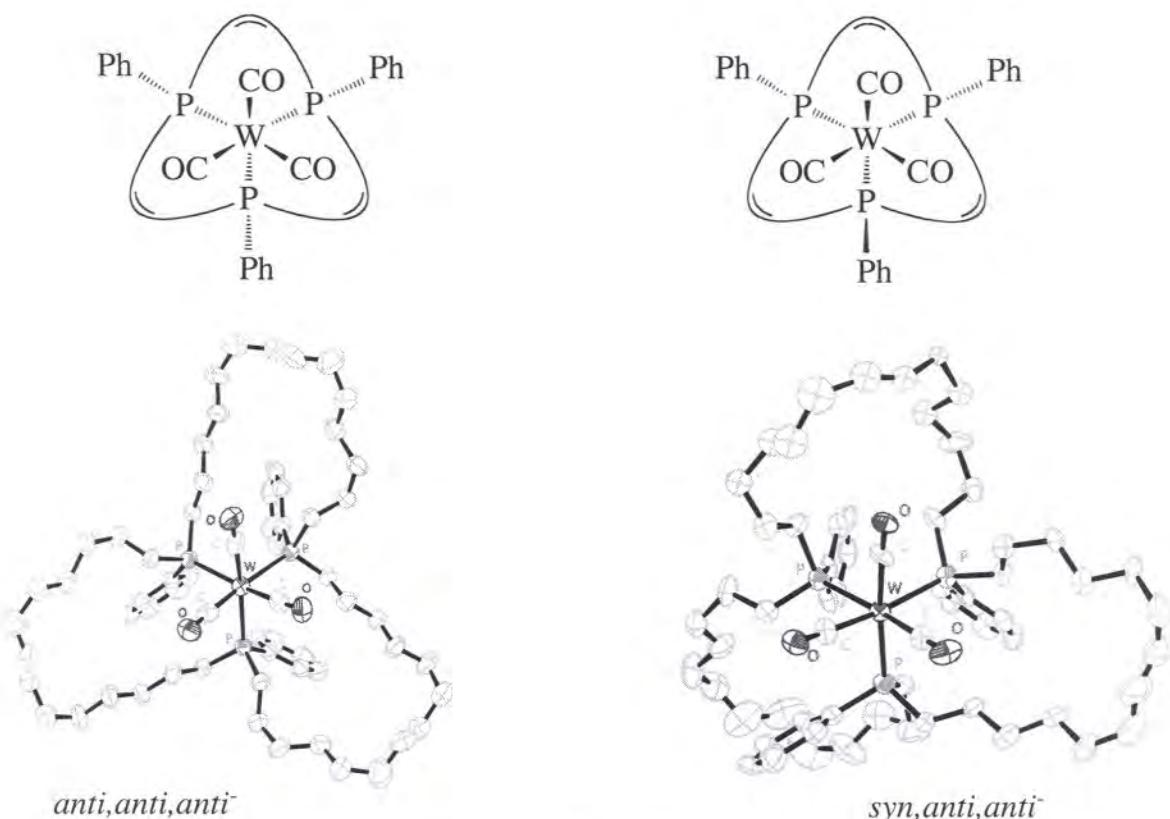
## ALKYNE METATHESIS in METAL COORDINATION SPHERES effect of catalyst



TRIPLE MACROCYCLIZATION to  
TRIPHOSPHINE, DIPHOSPHINE, and tris(MONOPHOSPHINE) COMPLEXES

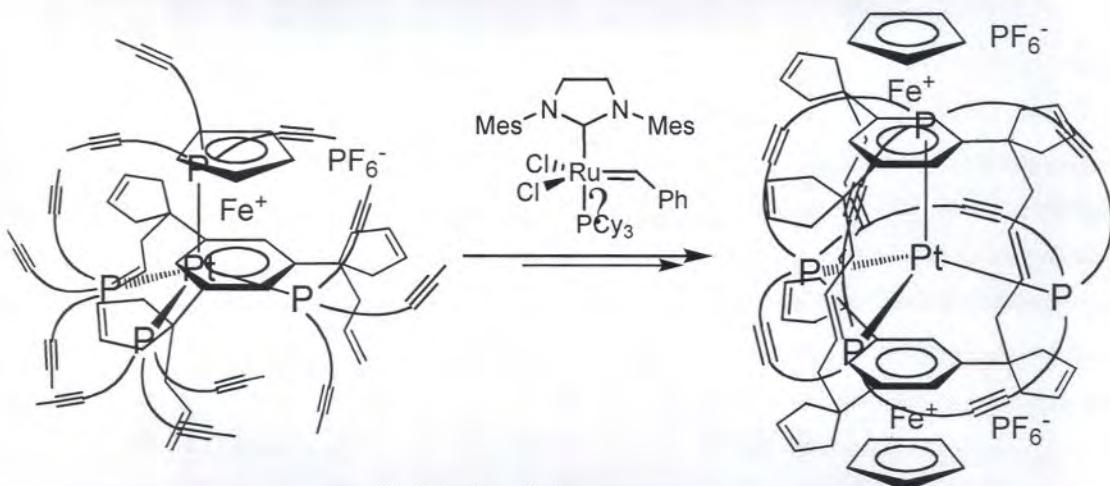


*NMR and mass spectra show no remaining  $=\text{CH}_2$   
 still a multitude of isomers after hydrogenation (94%)  
 mass spectra show all three types of ligands ( $\text{P}_3$ ,  $\text{P}_2$ ,  $\text{P}_1$ )*



Hydrogenation ( $\text{H}_2$  (90 psi) /  $(\text{Ph}_3\text{P})_3\text{RhCl}$  / toluene) leads to a mixture of isomers in 94% yield

CONCLUSION: ALKENE (AND ALKYNE) METATHESIS OFFERS  
INCREDIBLE OPPORTUNITIES FOR THE SYNTHESIS OF  
ARCHITECTURALLY NOVEL ORGANOMETALLIC COMPOUNDS



Martinez, V.; Blais, J.-C.; Astruc, D. *Angew. Chem. Int. Ed.* **2003**, 42, 4366.

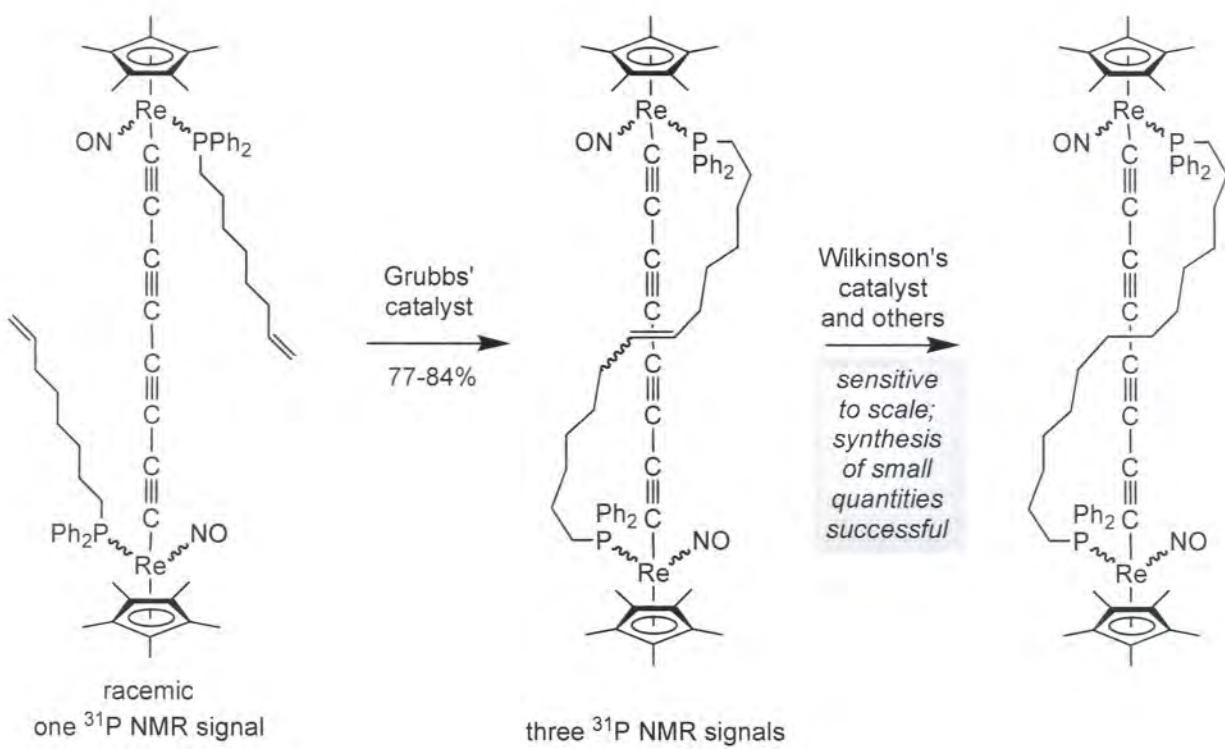
review: Bauer, E.; Gladysz, J. A. "Handbook of Metathesis", R. H. Grubbs, Ed. 2003

METATHESIS TEAM 2003-2004  
Mr. Eike Bauer and Dr. Takamori Shima

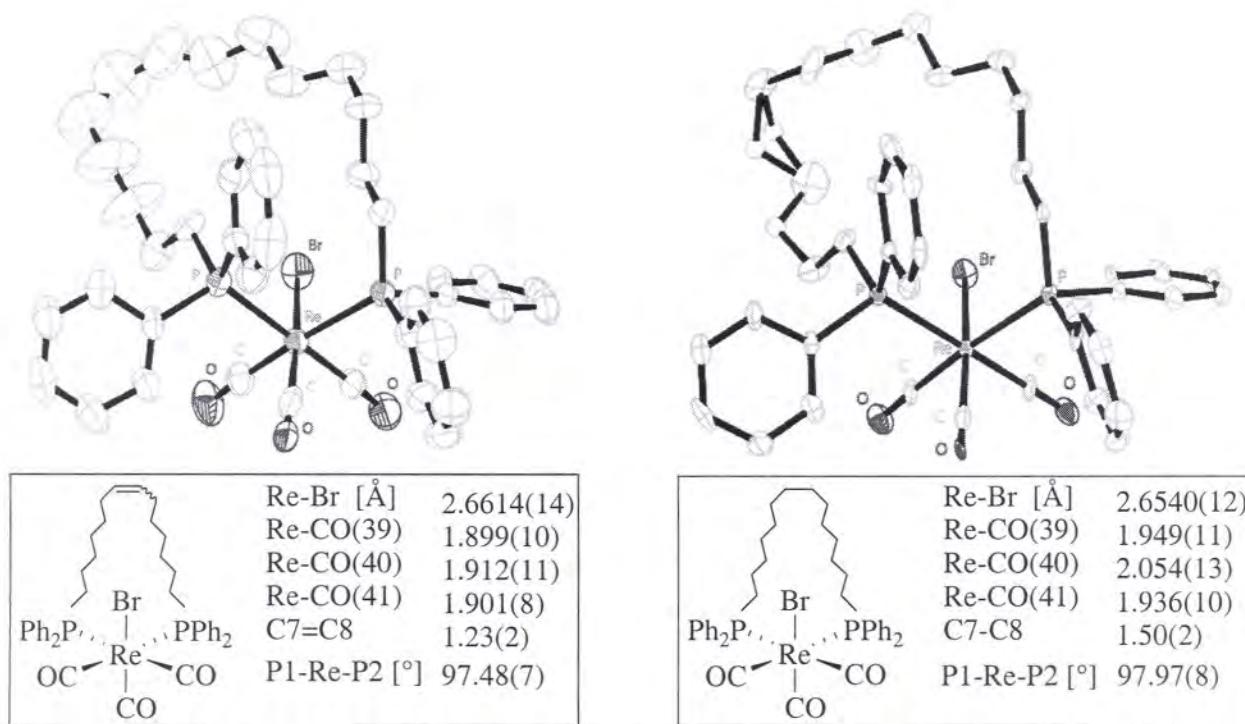


financial support: DFG

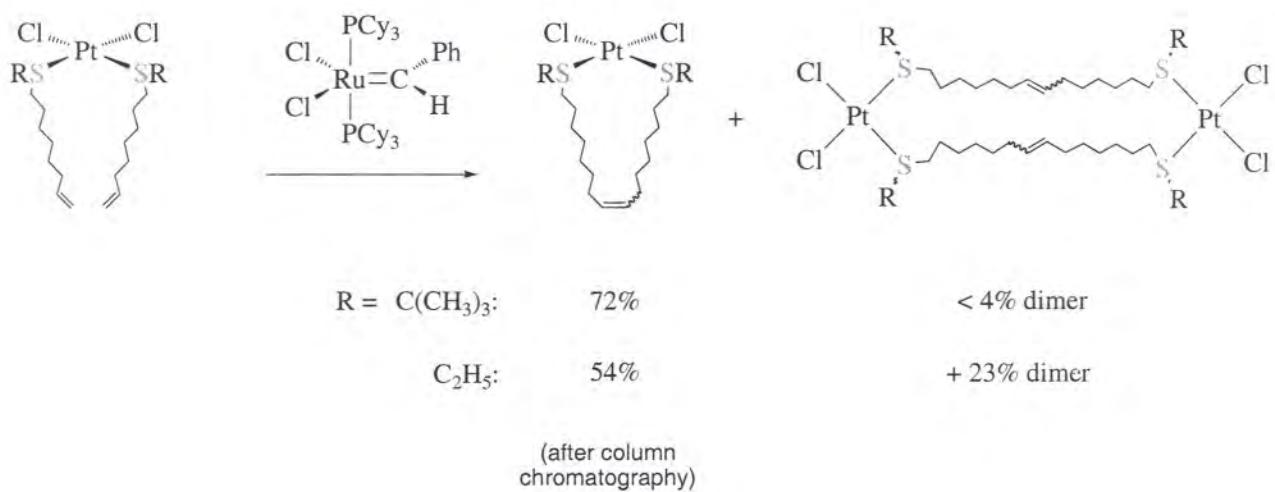
# POSSIBLE ROUTE to a DIRHENIUM "SINGLE HELIX"



# CRYSTAL STRUCTURES OF THE RHENAMACROCYCLES

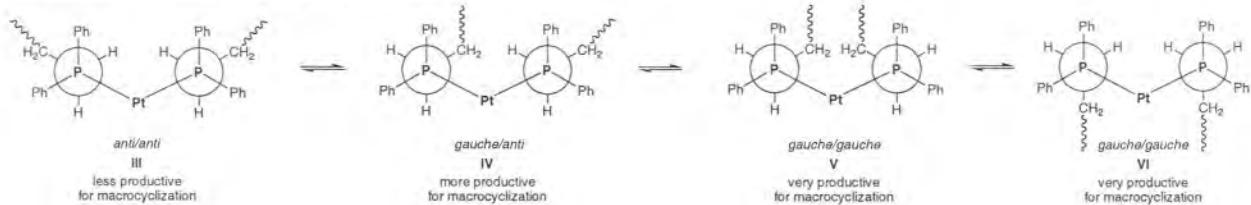


## CYCLIZATION WITHIN TWO *cis*-LIGANDS PLATINUM-THIOETHER MACROCYCLES

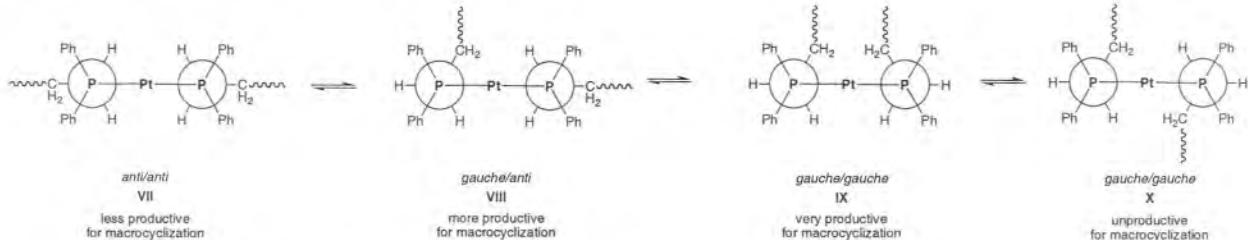


**Scheme 6.** Selected conformational equilibria.

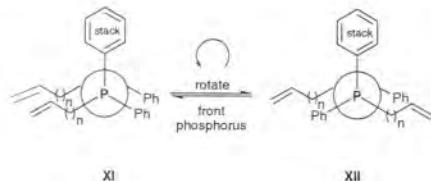
(A) Representative equilibria in *cis*-bis(phosphine) complex **12**



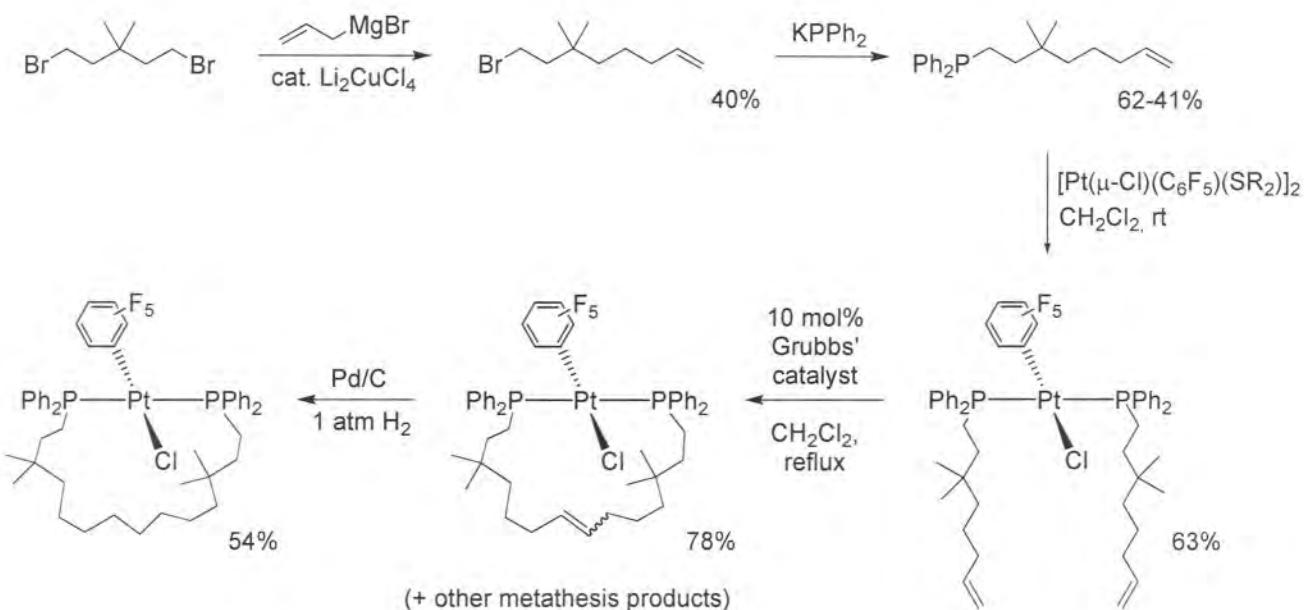
(B) Representative equilibria in *trans*-bis(phosphine) complexes **3a-e**.



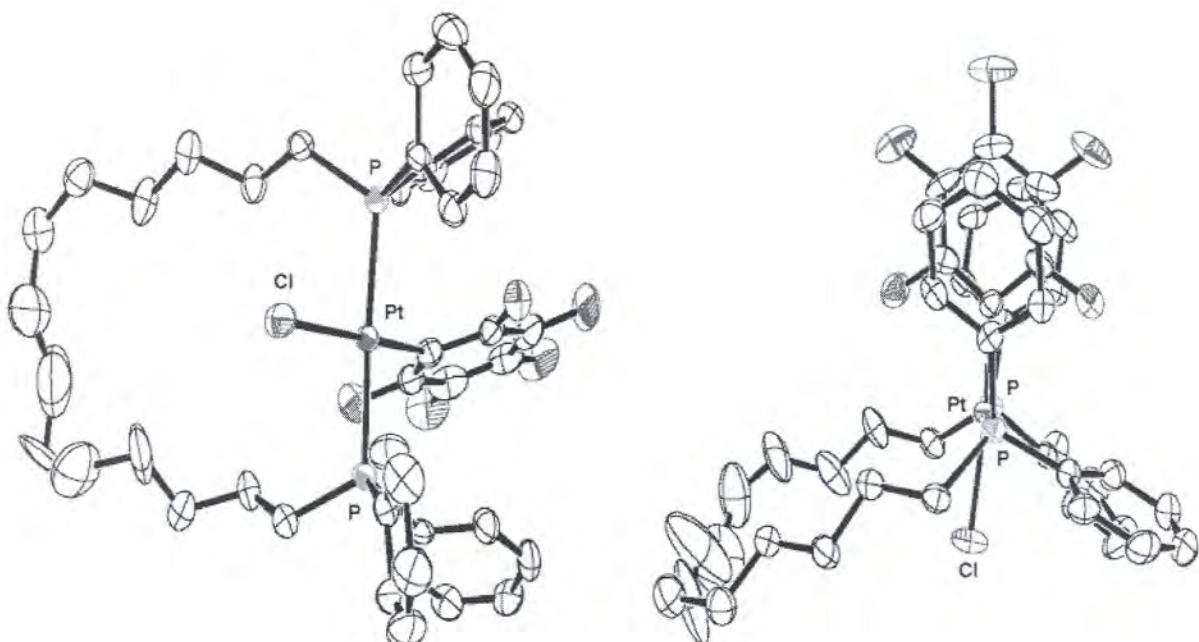
(C) Equilibria for *trans*-bis(phosphine) complexes **3a-e** with C<sub>6</sub>H<sub>5</sub>/C<sub>6</sub>F<sub>5</sub>/C<sub>6</sub>H<sub>5</sub> stacks.



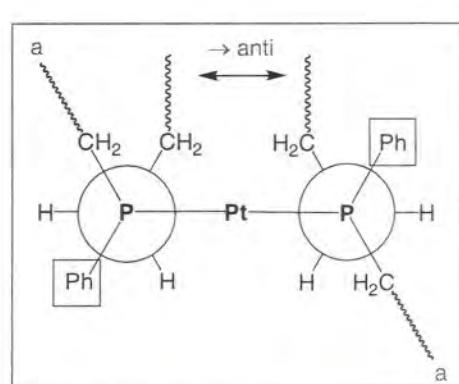
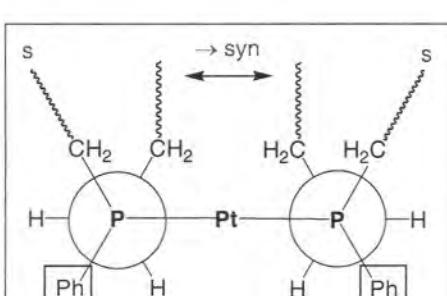
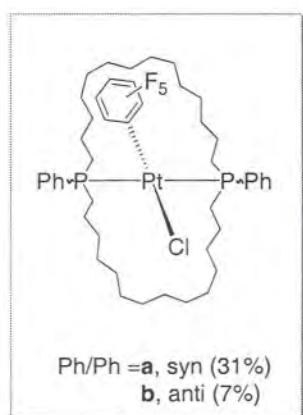
## MACROCYCLIZATION of a SUBSTRATE with GEMINAL DIMETHYL GROUPS



# CRYSTAL STRUCTURE of TRANS-SPANNING PHOSPHINE COMPLEX



## THE FIRST CH=CH<sub>2</sub>/CH=CH<sub>2</sub> METATHESIS SETS THE SYN/ANTI MANIFOLD



mass spectrometry of the crude reaction mixture shows some diplatinum product

the anti manifold may be more oligomerization prone