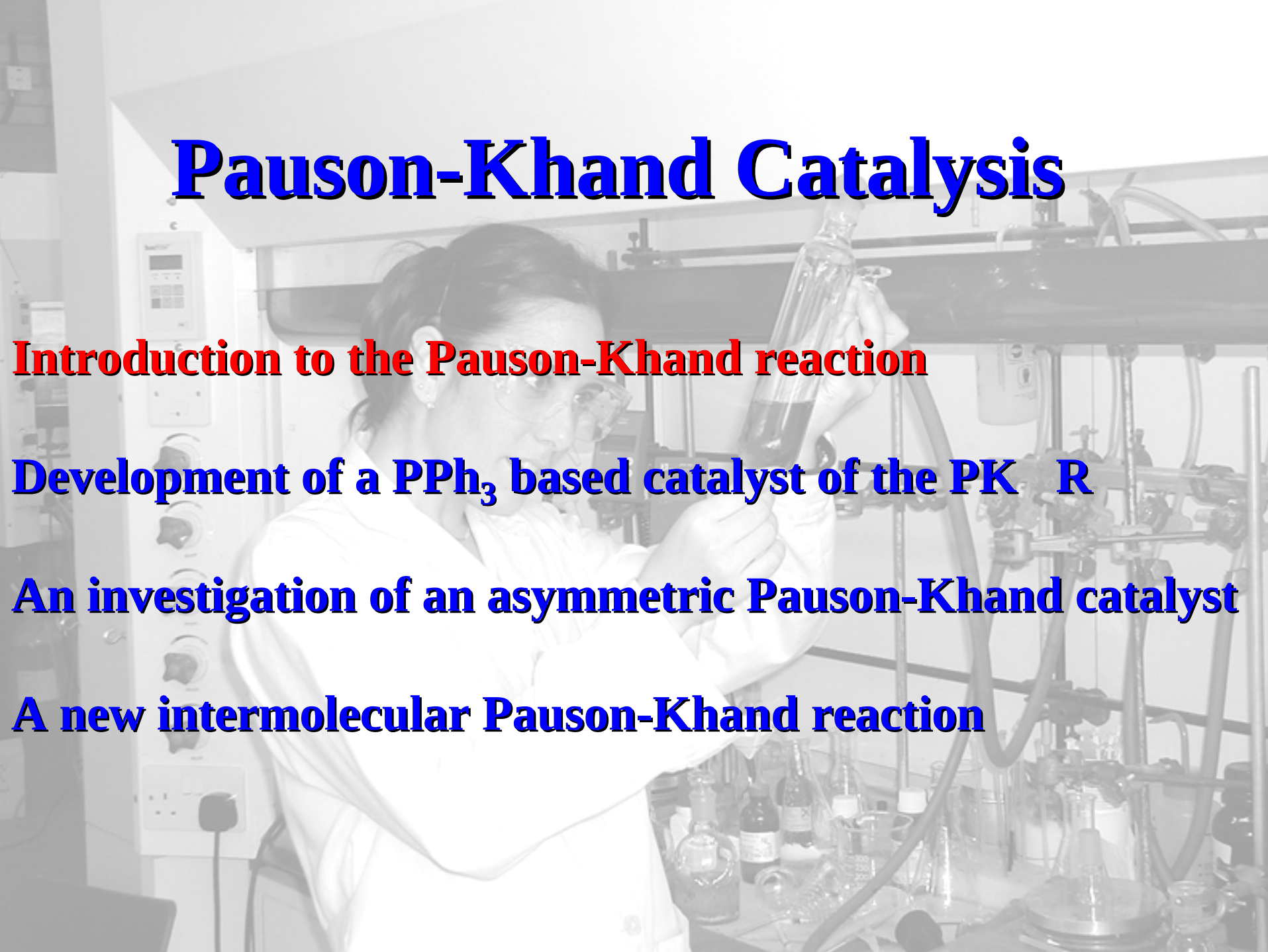
Pauson-Khand Catalysis



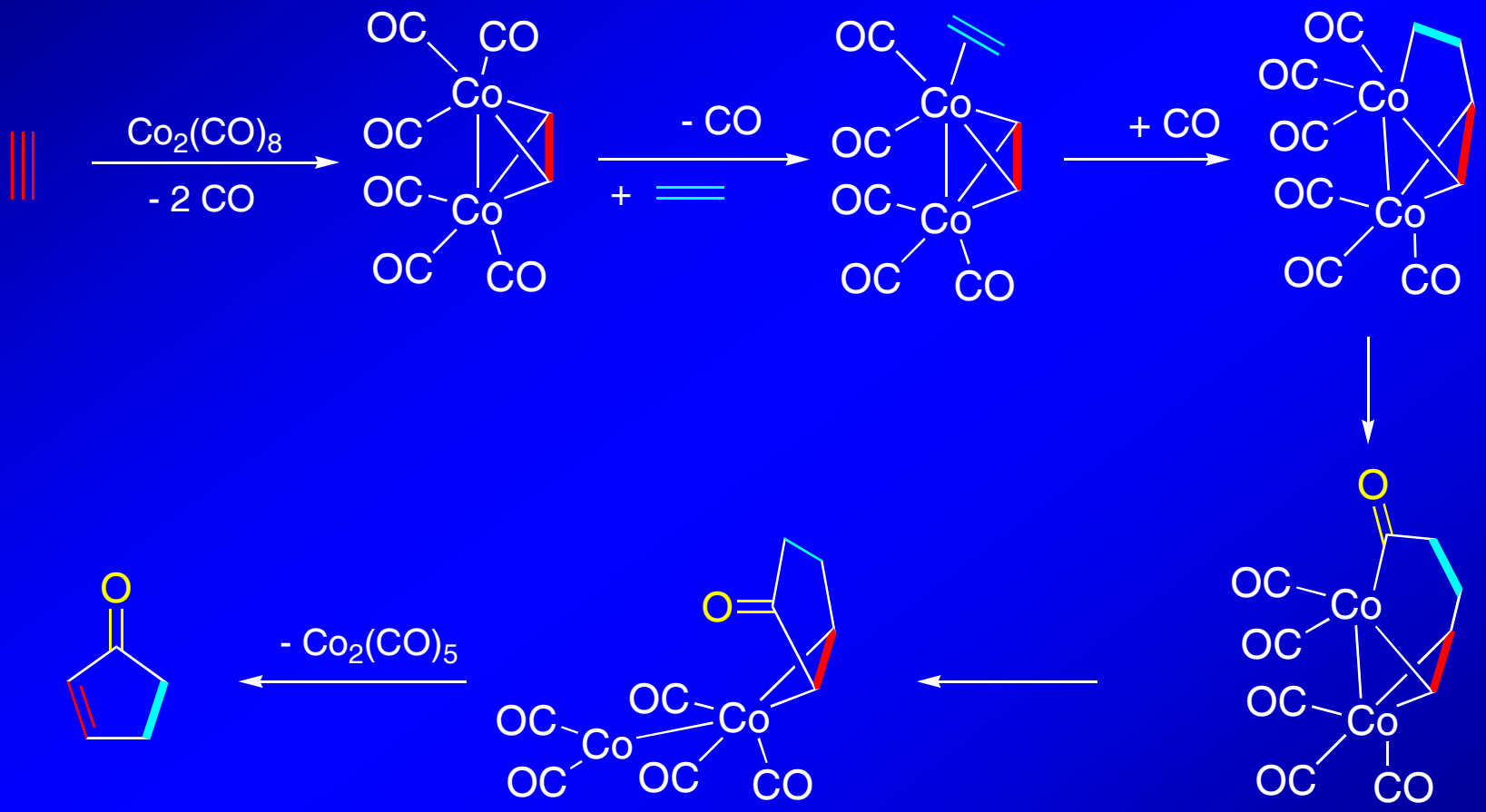
Introduction to the Pauson-Khand reaction

Development of a PPh_3 based catalyst of the PK R

An investigation of an asymmetric Pauson-Khand catalyst

A new intermolecular Pauson-Khand reaction

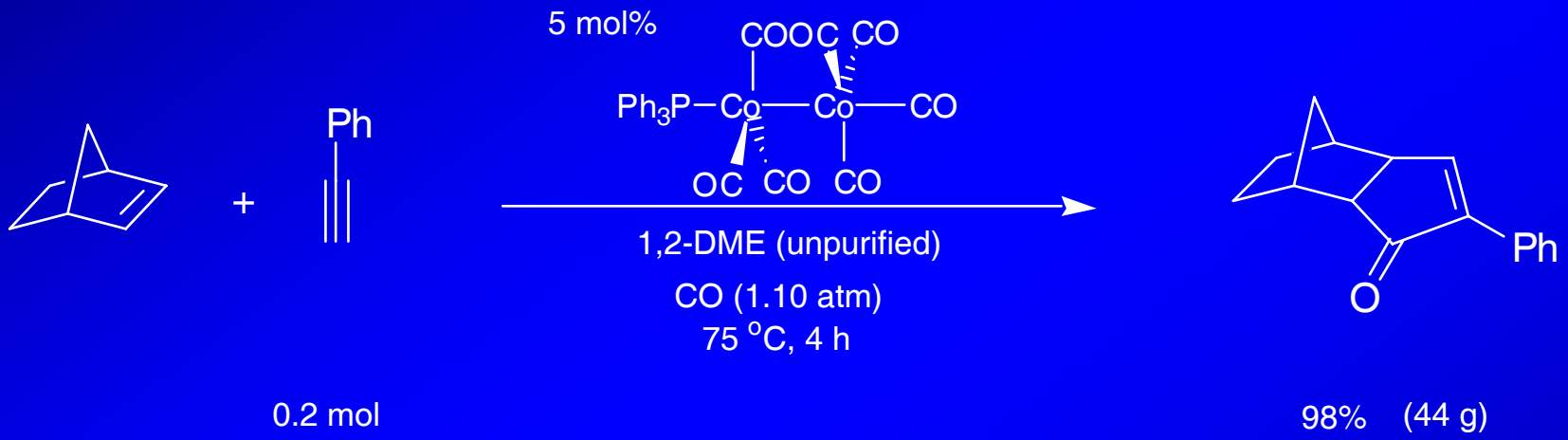
Magnus' mechanism for the stoichiometric PKR



P. Magnus and L.M. Principe, *Tetrahedron Lett.*, 1985, **26**, 4851

For density functional studies, see M. Yamanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2001, **123**, 1703

Catalyst operates on relatively large scale



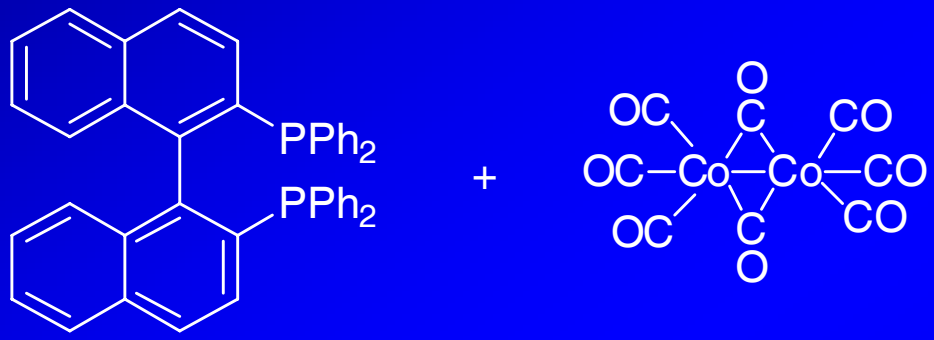
0.2 mol

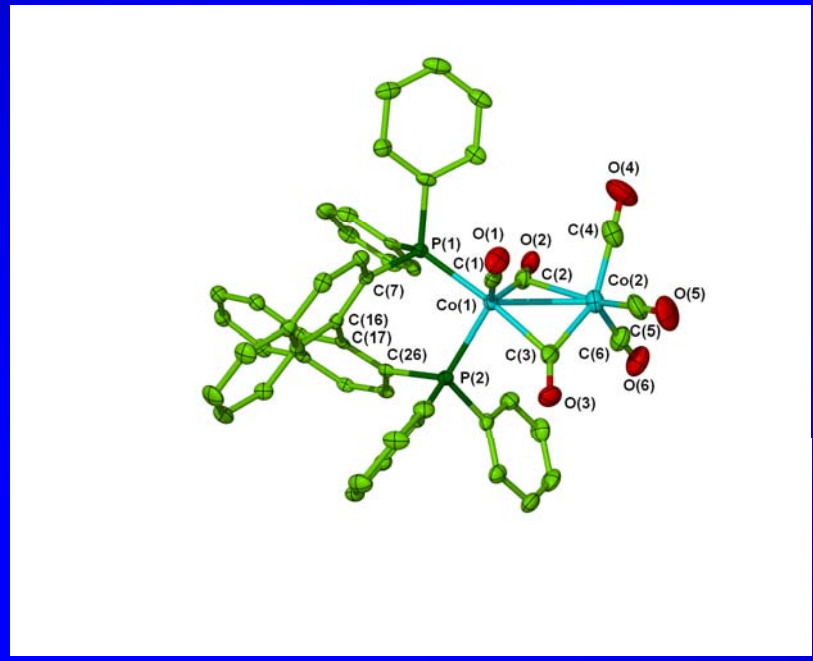
98% (44 g)

S.E. Gibson, C. Johnstone, A. Stevenazzi,
Tetrahedron **2002**, *58*, 4937-4942

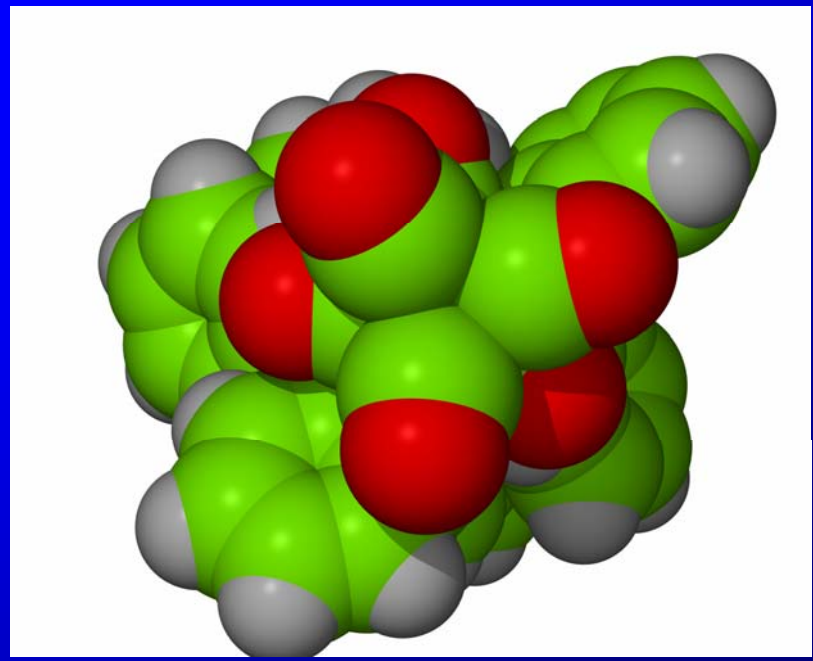
For a review of the catalytic Pauson-Khand reaction see:
S.E. Gibson, A. Stevenazzi,
Angew. Chem. Int. Edn. 2003, *42*, 1800-1810

How does BINAP bind to octacarbonyldicobalt(0)?

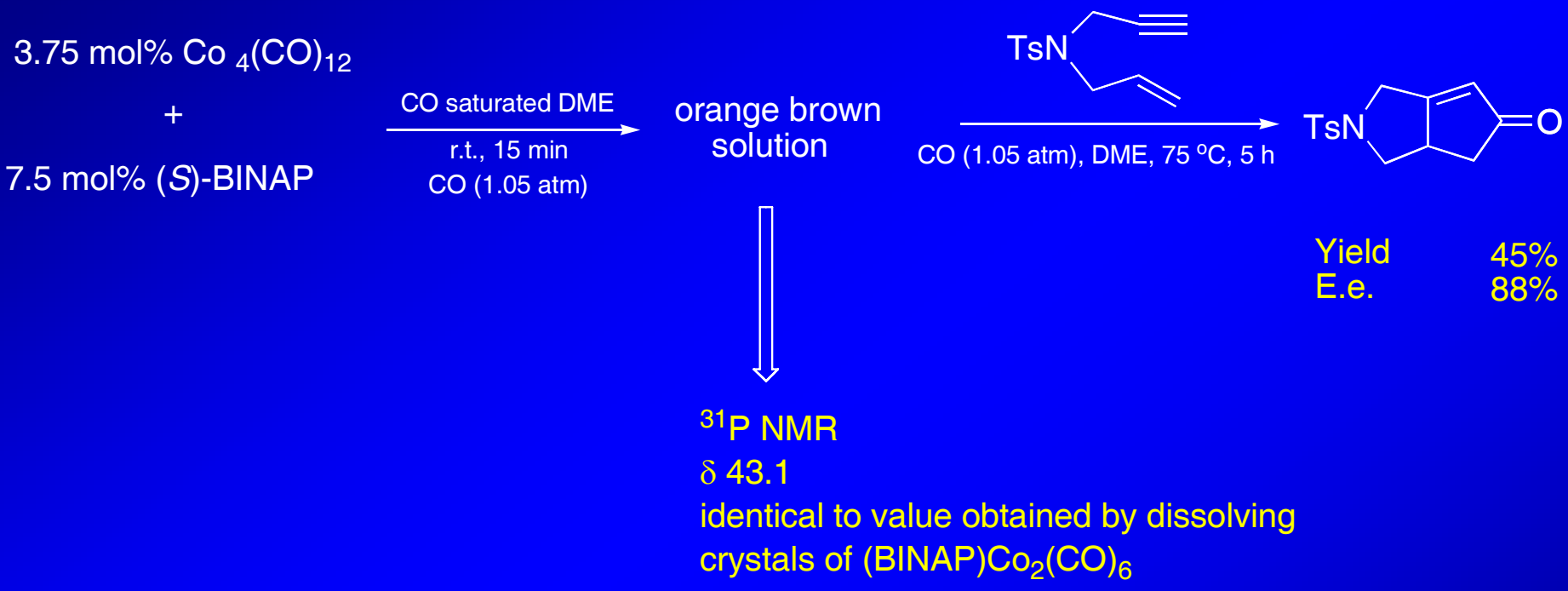




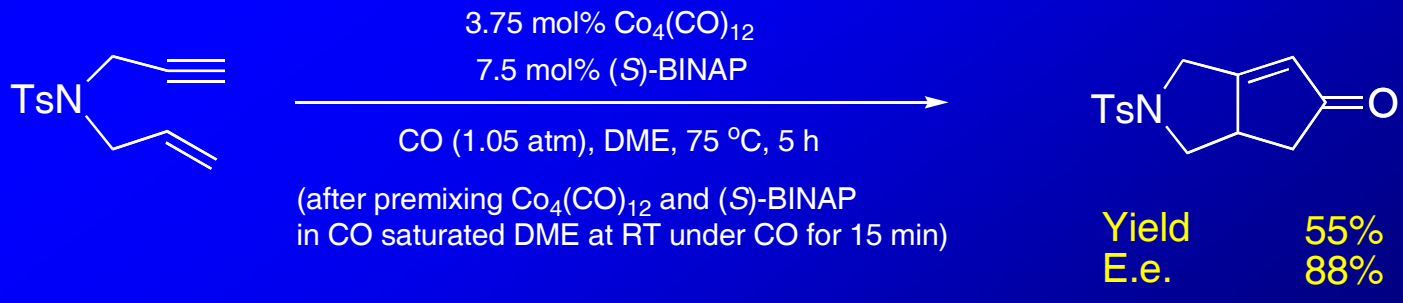
dark red crystals



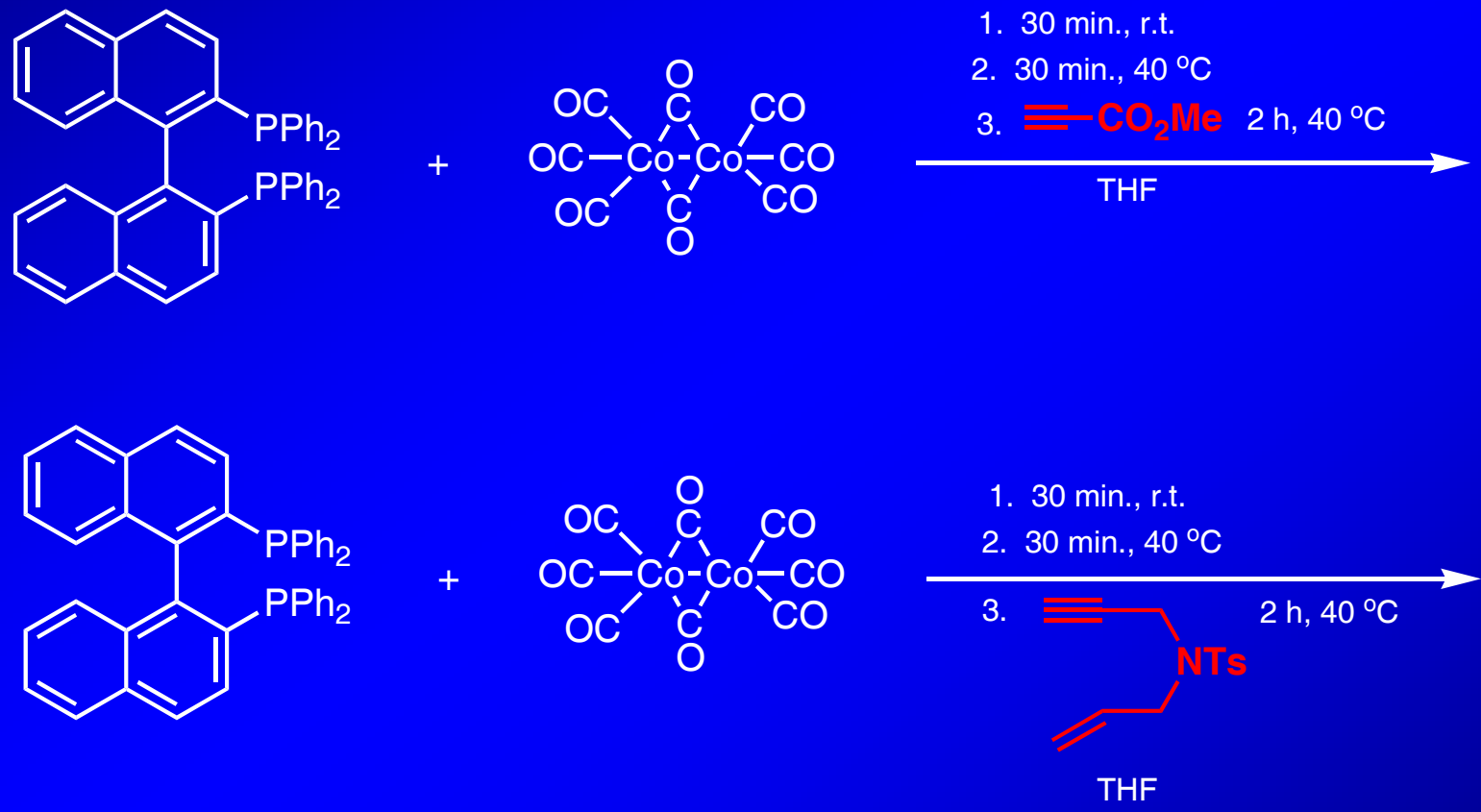
Solution studies confirm key pre-catalyst



Earlier result:

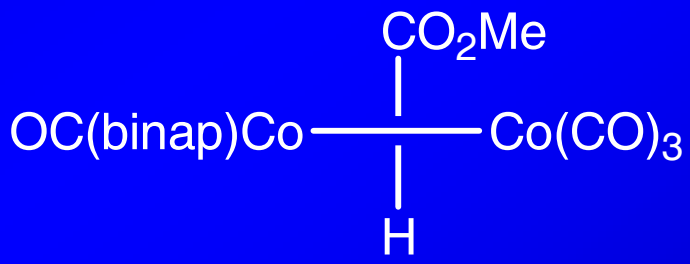


Do alkynes form complexes?

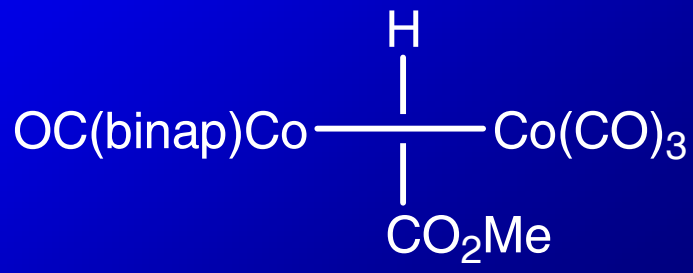


Structure of two isomers

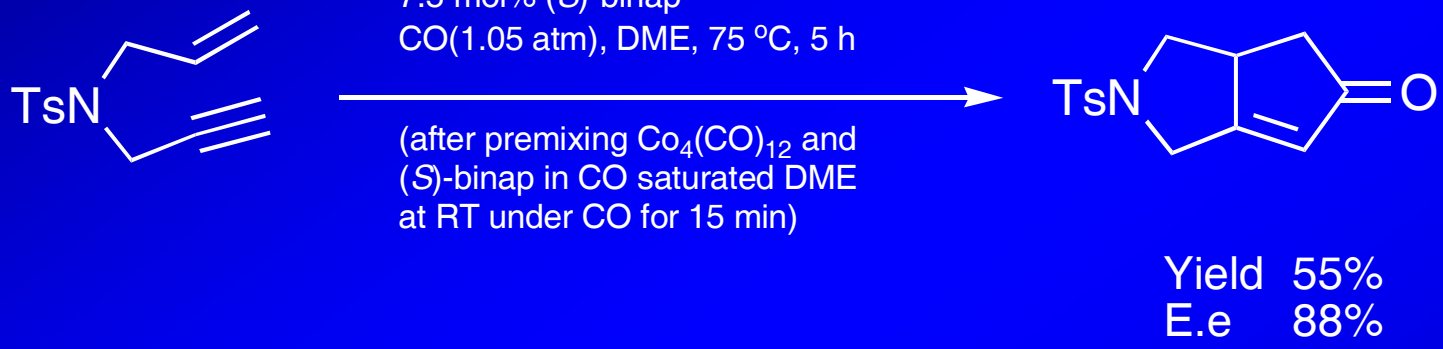
major

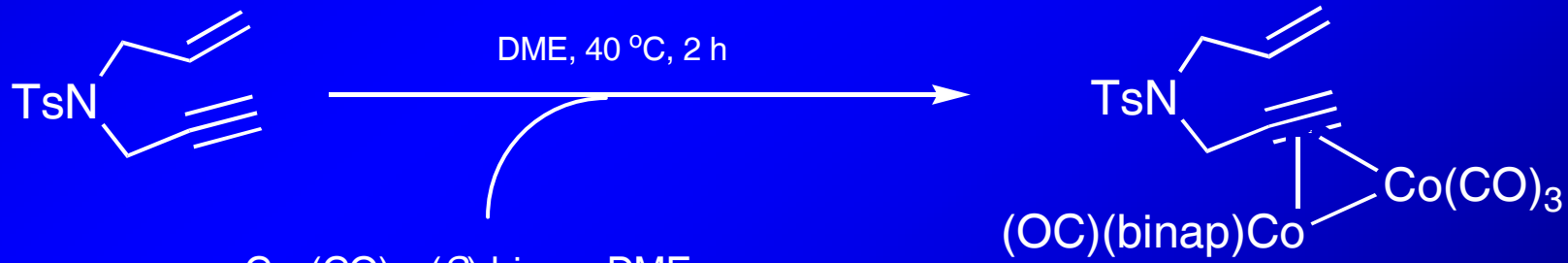


minor



Isomer ratio and e.e. do not match





Isomerisation is faster under CO than N_2 at 75 °C and 60 °C

QuickTime™ and a
GIF decompressor
are needed to see this picture.

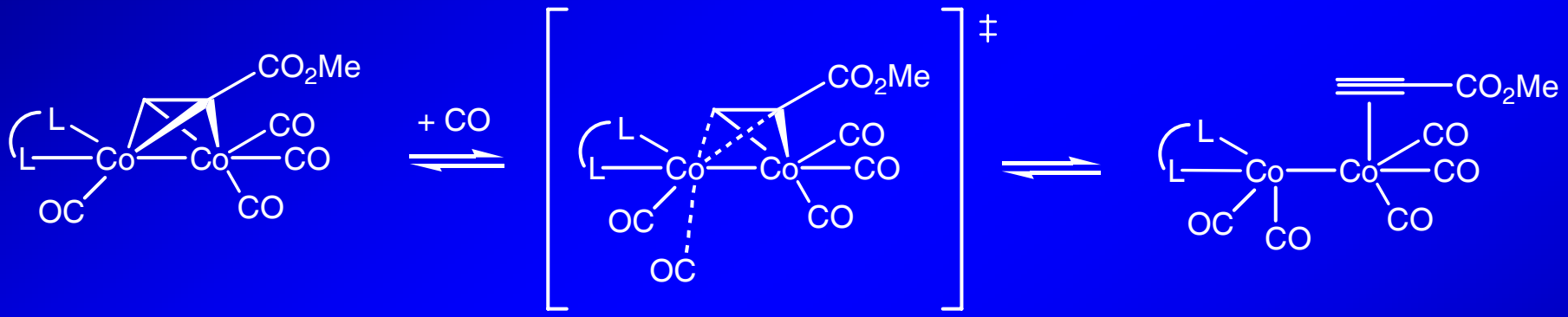
Inverse gated ^{31}P NMR isomerisation experiments starting with major isomer

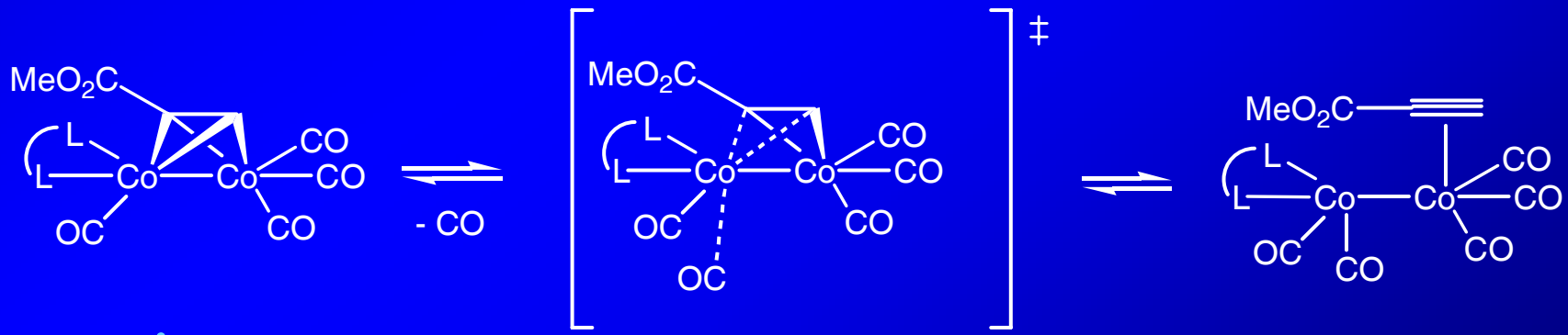
Diamond, — CO / 75 °C. Triangle, ----, N_2 / 75 °C. Square, ·····, CO / 60 °C. Cross, ·–·–, N_2 / 60 °C.

S.E. Gibson, K.A.C. Kaufmann, J.A. Loch, J.W. Steed, A.J.P. White, *Chem. Eur. J.* **2005**, *11*, 2566-2576

Alkyne rotation pathway

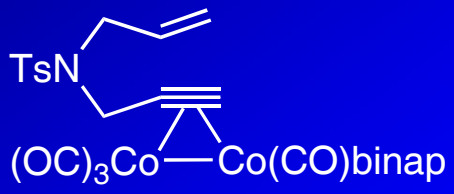
major





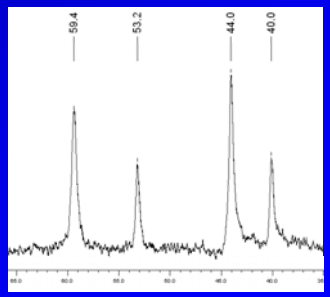
minor

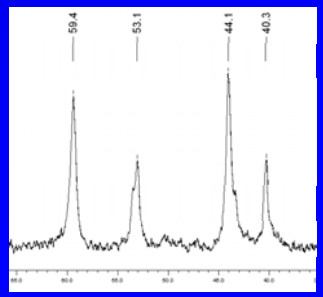
A ^{31}P NMR study of enyne complexes

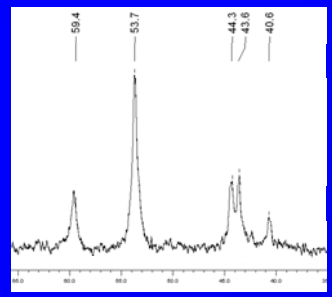


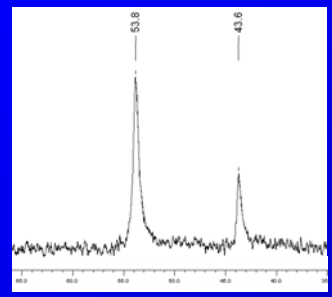
^{31}P NMR spectra run at
5 °C or 10 °C intervals between 30 °C and 75 °C
and afterwards at 30 °C

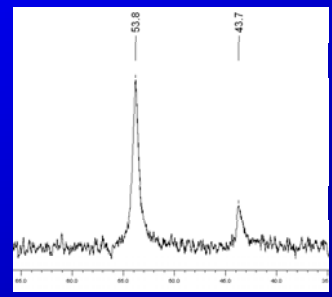
DME / CO









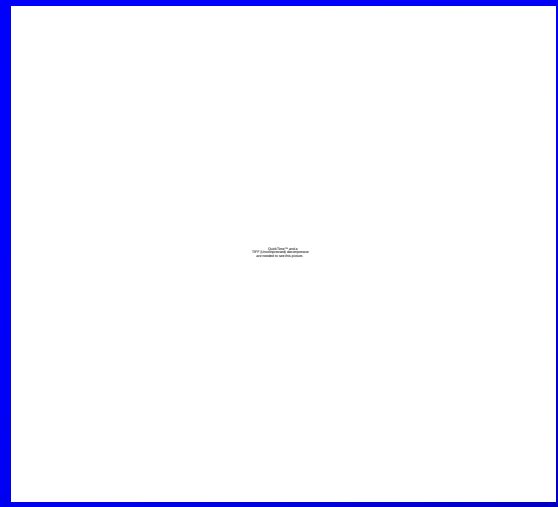


30 °C 45 °C 50 °C 60 °C 75 °C

S.E. Gibson, K.A.C. Kaufmann, P.R. Haycock, A.J.P. White, D.J. Hardick, M.J. Tozer, manuscript submitted

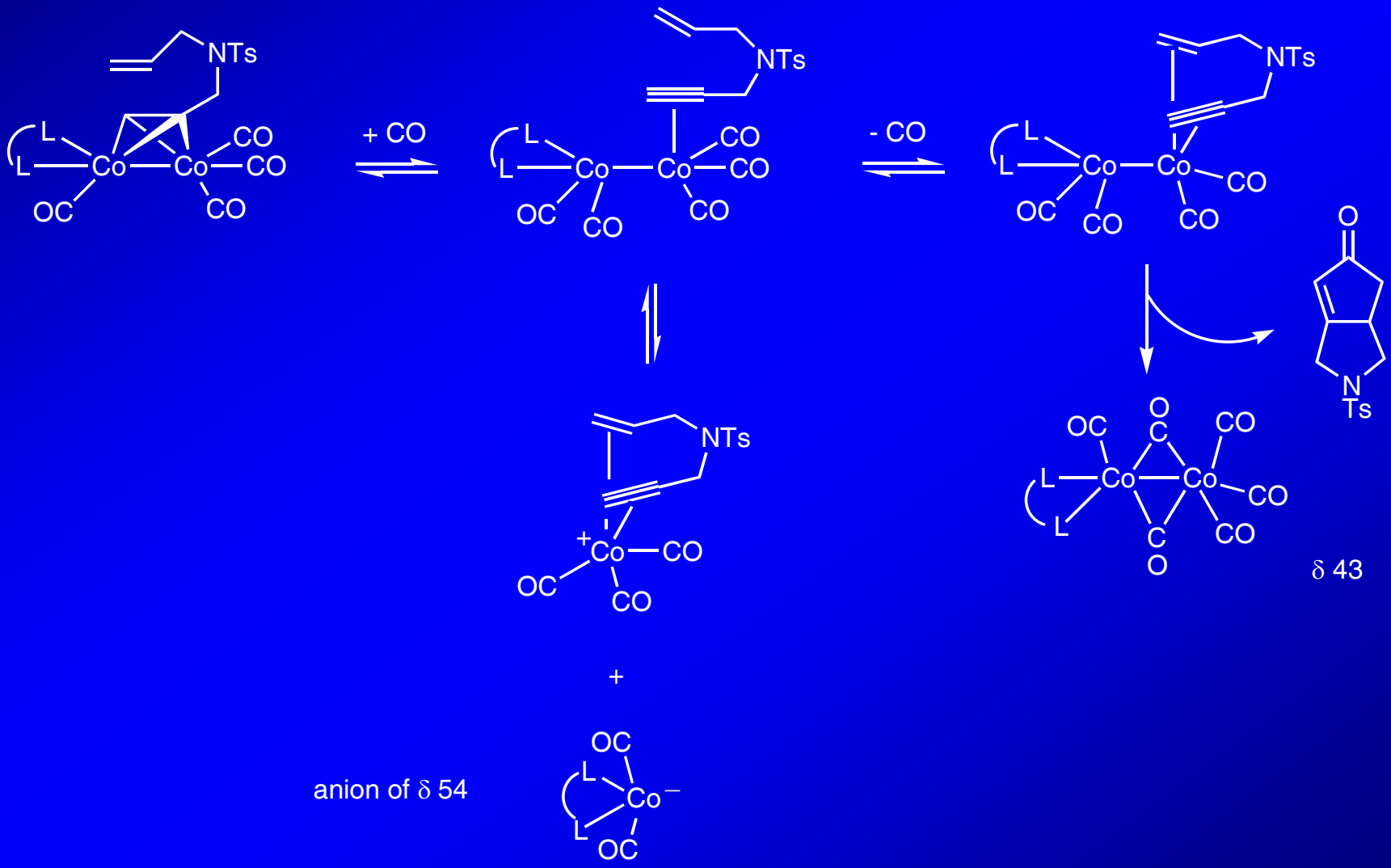
What is δ54?

Standard NMR sequence (DME) → ^{31}P NMR: δ 54, 43 →

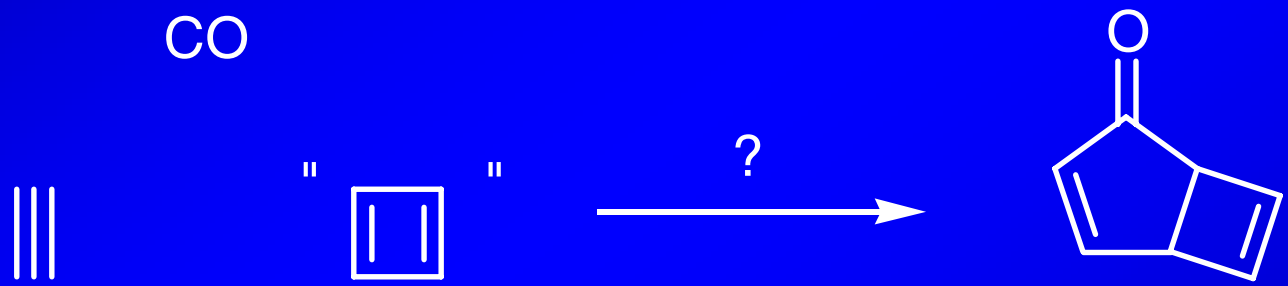


Standard NMR sequence (d^8-THF) → ^{31}P NMR: δ 54, 43 → ^{1}H NMR: δ -11.6

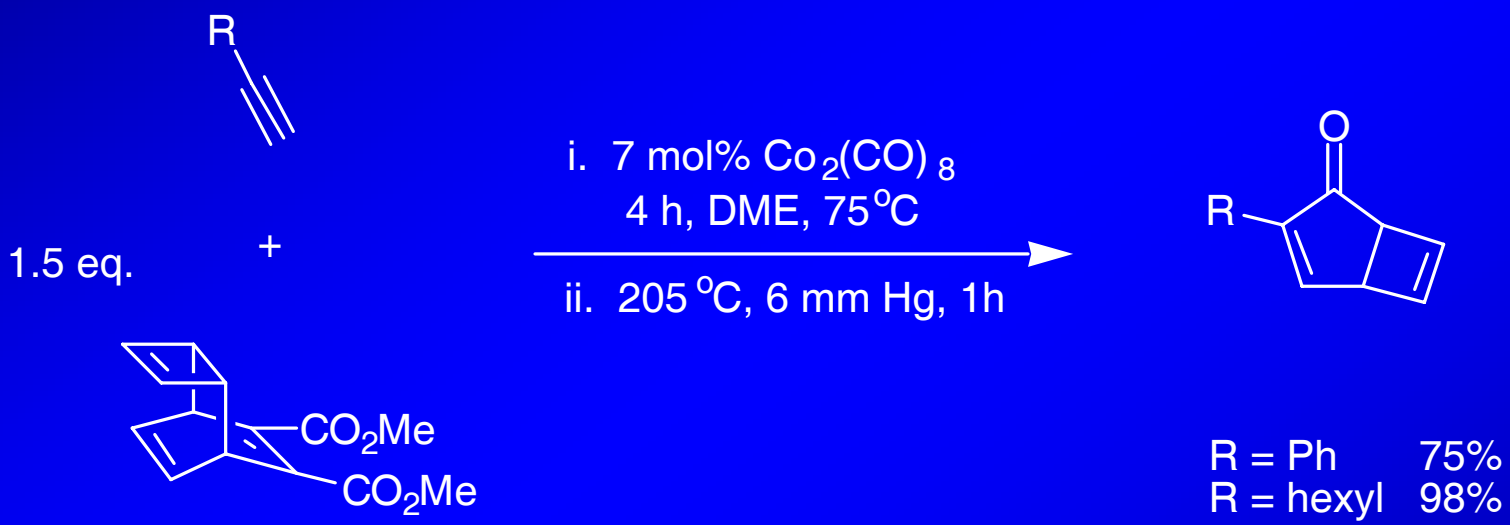
Proposed pathways to δ 54 and δ 43



Use of ‘cyclobutadiene’ in PKR?

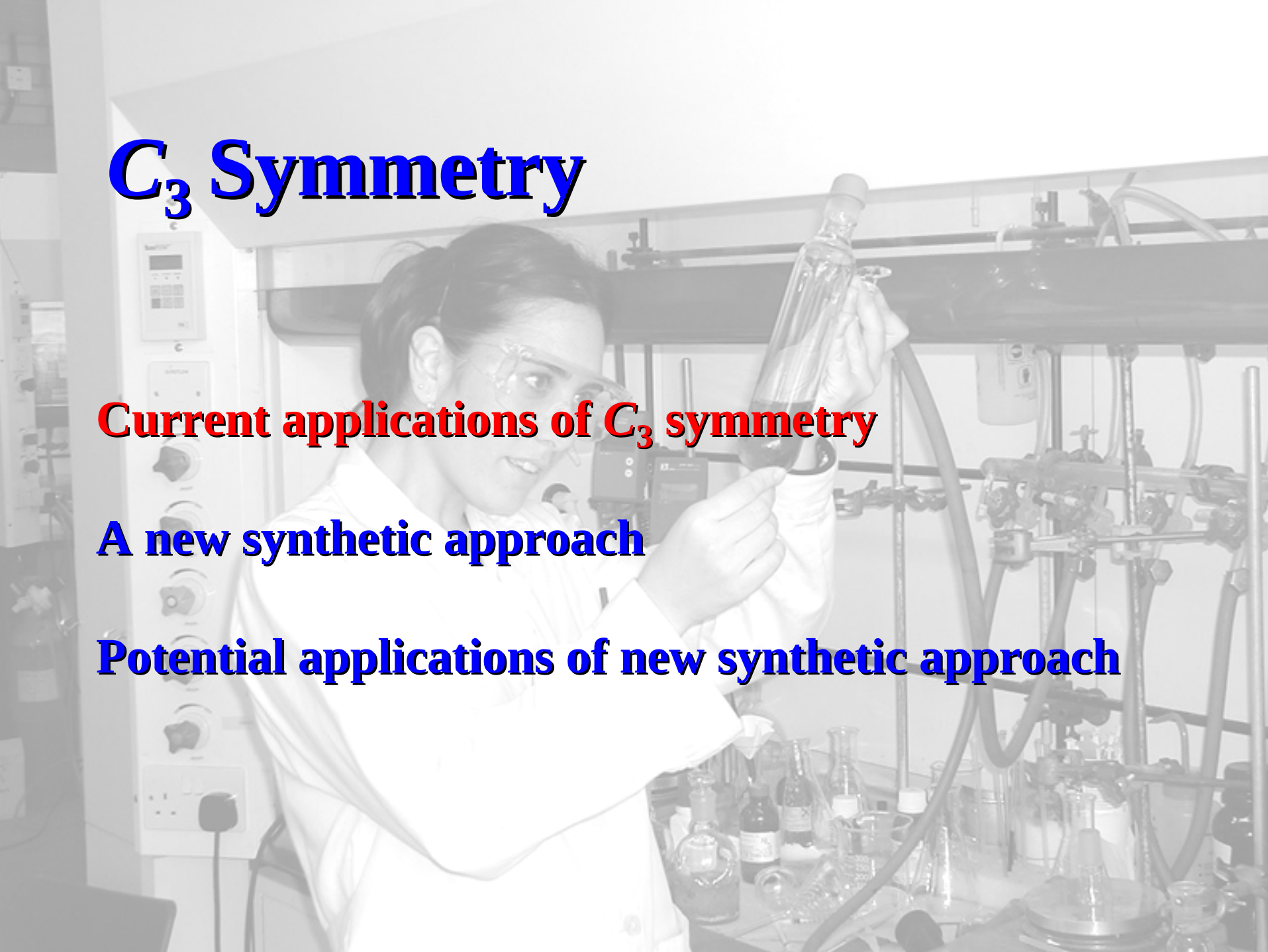


Catalytic cyclobutadiene PKR avoiding intermediate isolation



S.E. Gibson, N. Mainolfi, S.B. Kalindjian, P.T. Wright, *Angew. Chem. Int. Edn.*, **2004**, *43*, 5680-2.

C_3 Symmetry



Current applications of C_3 symmetry

A new synthetic approach

Potential applications of new synthetic approach

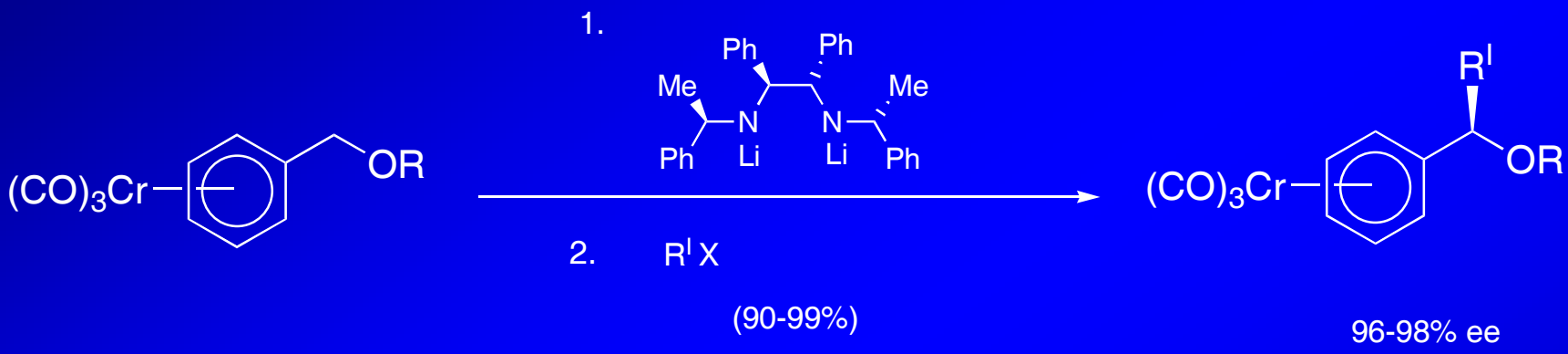
Natural and unnatural symmetry

A Trillium flower

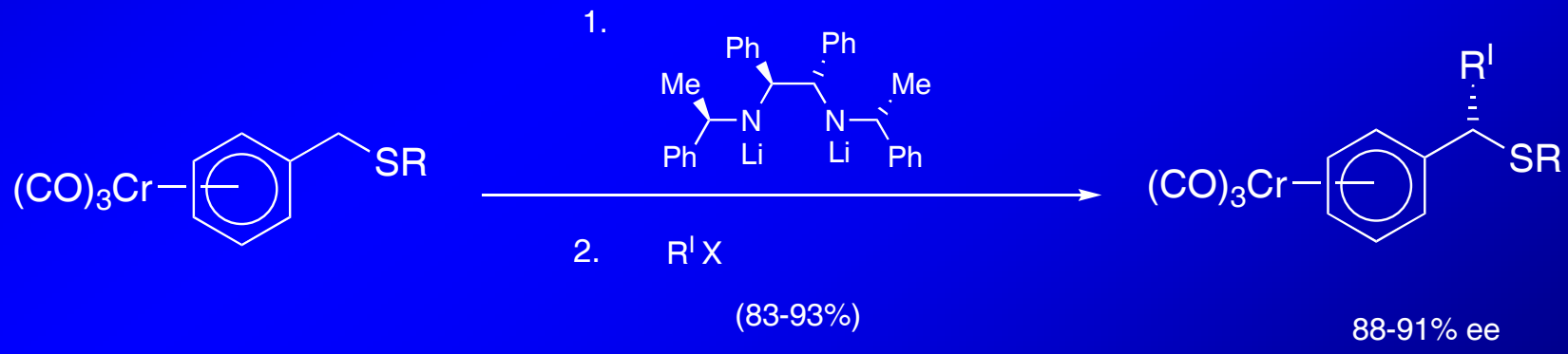
The Borromean rings

For a review of applications of C_3 symmetry,
M.P. Castaldi, S.E. Gibson, *Chem. Commun*. **2006**, 3045-3062
For a Highlight of recent developments in the area,
M.P. Castaldi, S.E. Gibson, *Angew. Chem*. **2006**, *45*, 4718-4720

A selective chiral base reaction

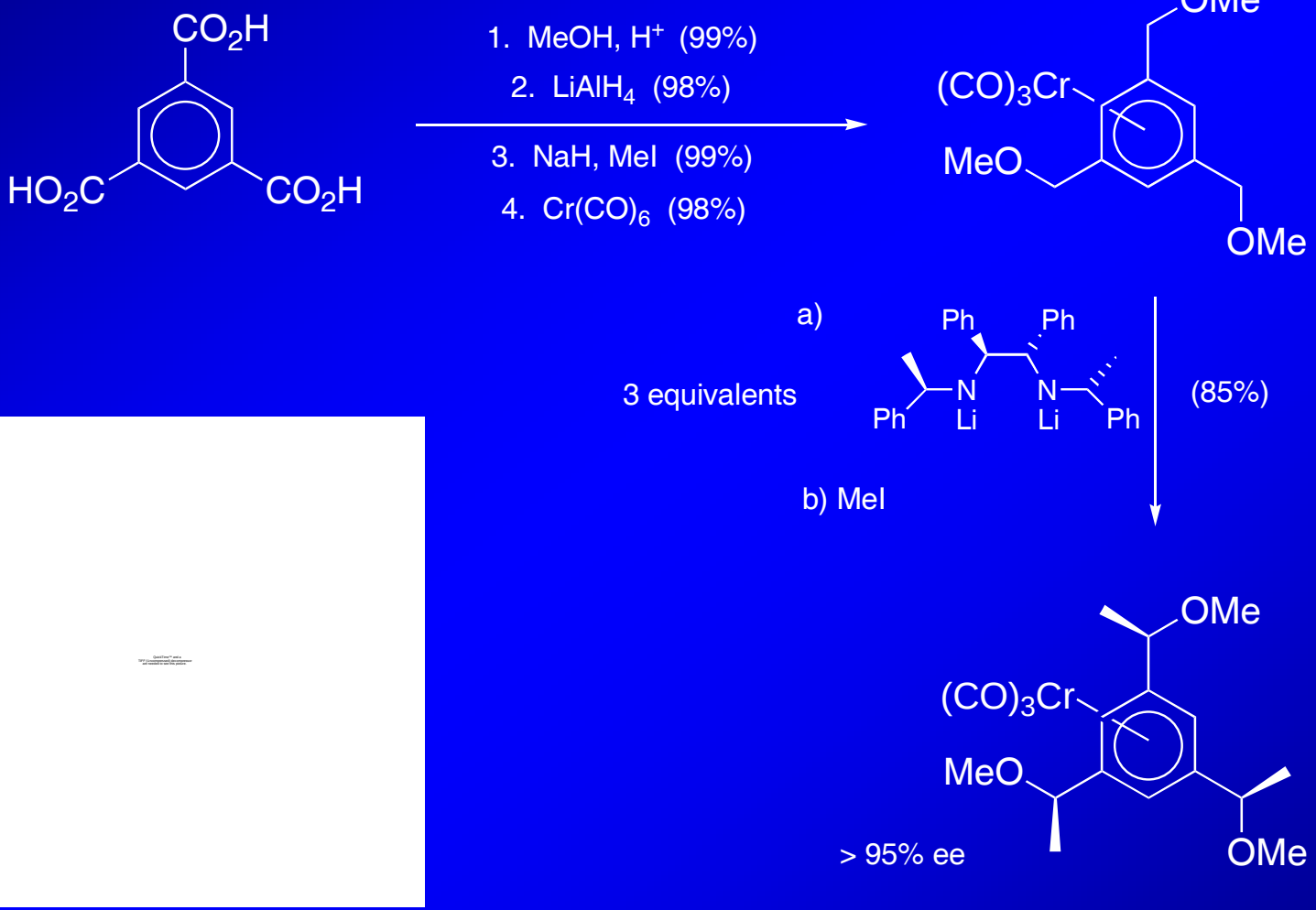


E.L.M. Cowton, S.E. Gibson, M.J. Schneider, M.H. Smith,
Chem. Commun. **1996**, 839-840



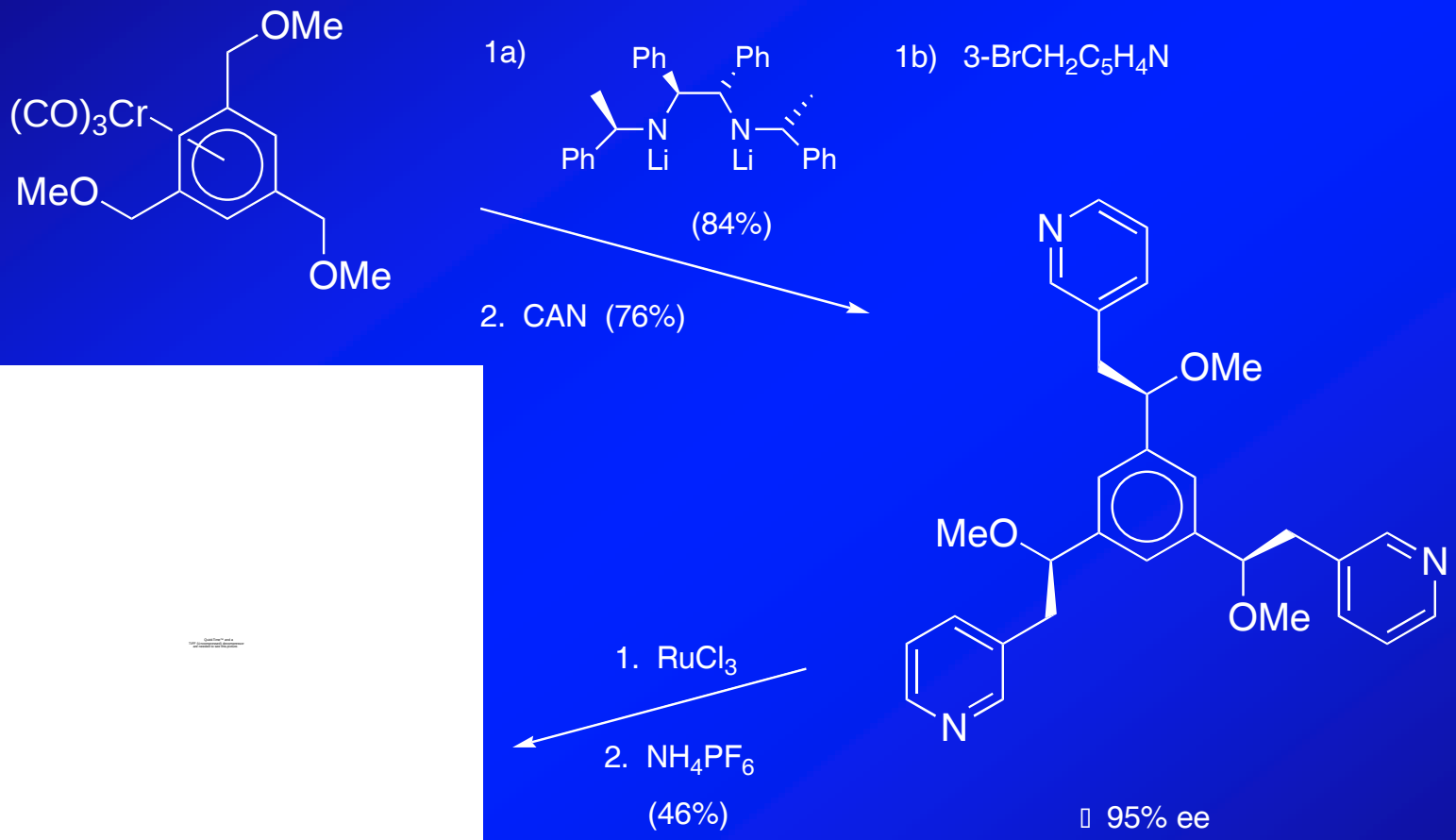
S.E. Gibson, P. Ham, G.R. Jefferson, M.H. Smith,
J. Chem. Soc., Perkin Trans. 1 **1997**, 2161-2

Introduction of three methyl groups



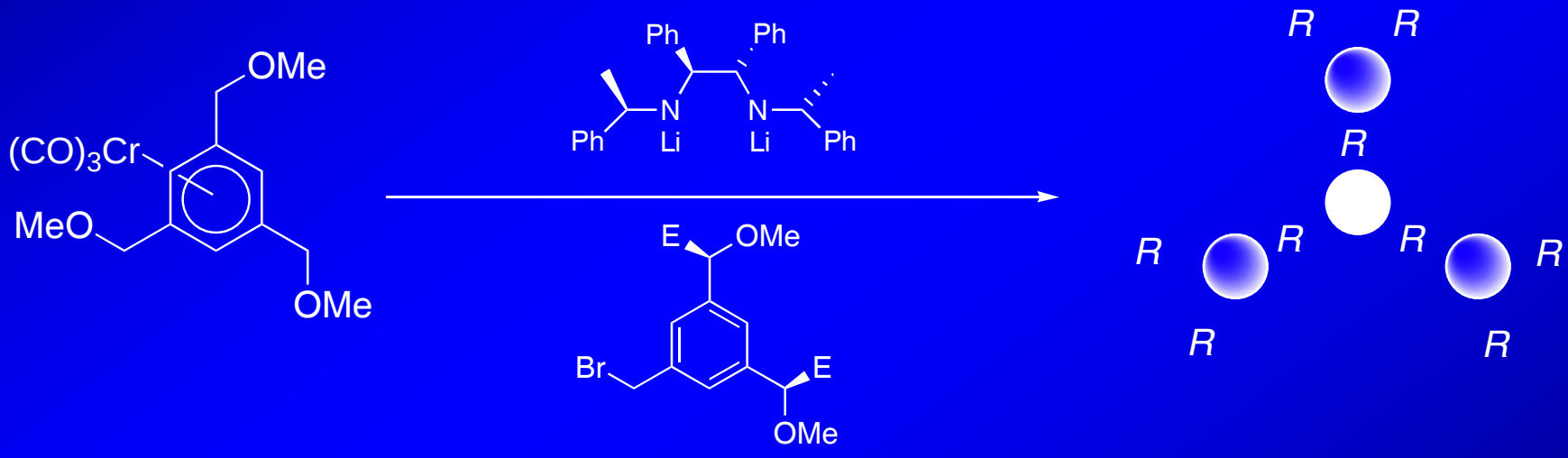
M.P. Castaldi, S.E. Gibson, M. Rudd, A.J.P. White, *Angew. Chem. Int. Ed*. **2005**, *44*, 3432-3435

A tris-pyridine ligand…..

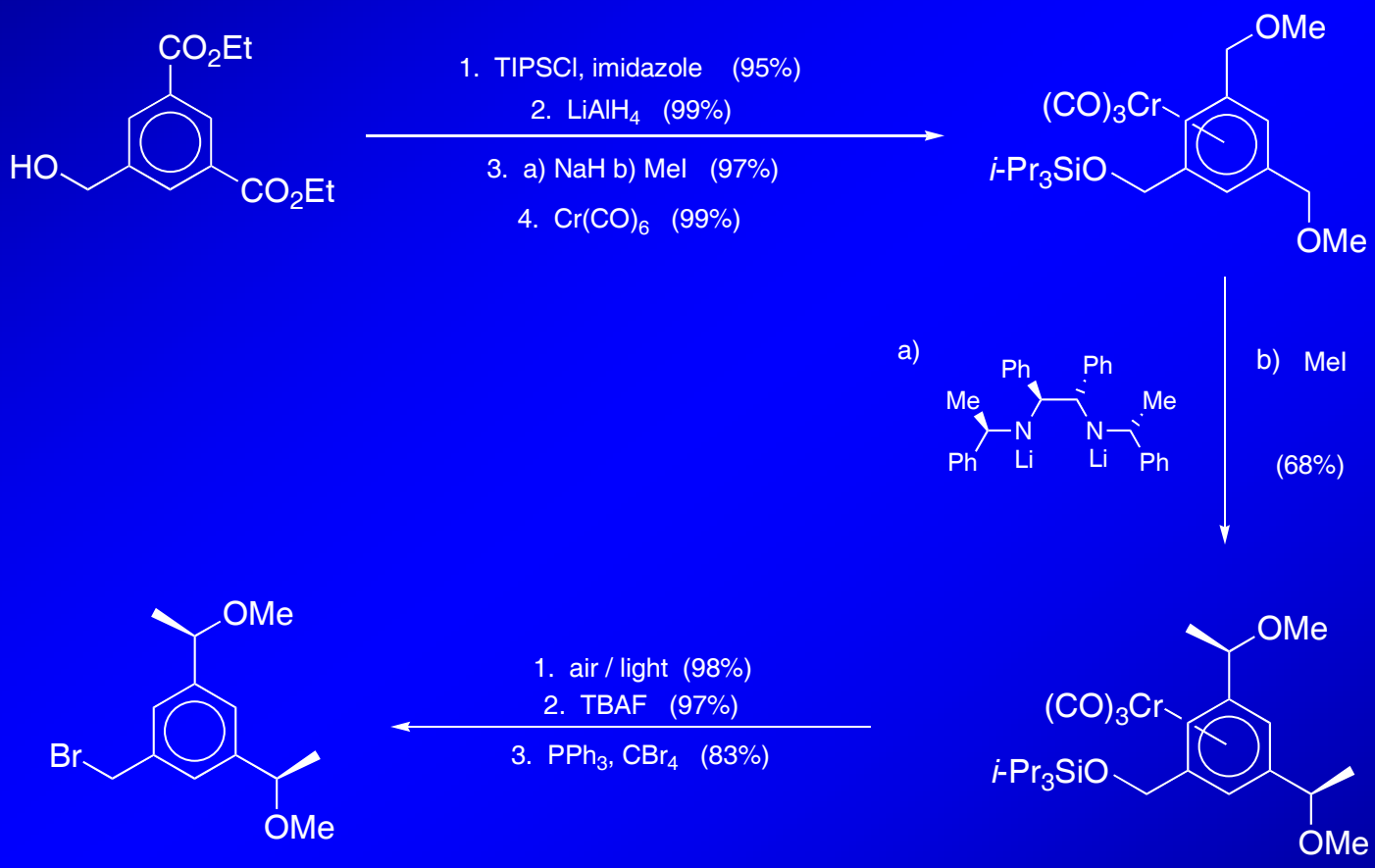


M.P. Castaldi, S.E. Gibson, M. Rudd, A.J.P. White, *Angew. Chem.* **2005**, *44*, 3432-3435;
M.P. Castaldi, S.E. Gibson, M. Rudd, A.J.P. White, *Chem. Eur. J.* **2006**, *12*, 138-148.

Control of inner stereochemistry

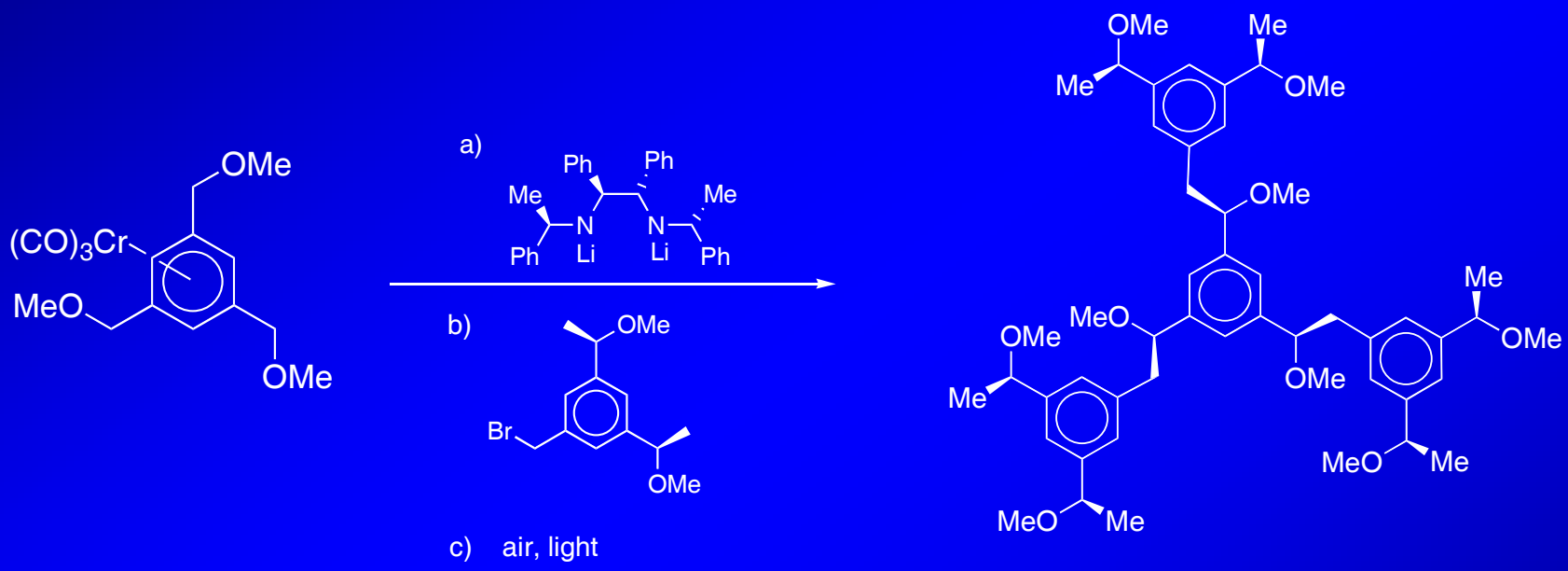


Synthesis of electrophile to give R_{outer}



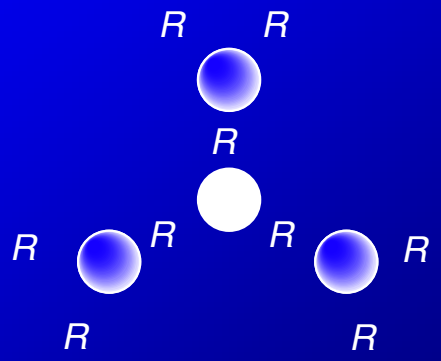
S.E. Gibson, J. Rendell, A. Drake, manuscript in preparation

Construction of molecule with $R_{inner}R_{outer}$



(55%)

(S_{inner} S_{outer}: 75%)



Four stereoisomers and their CD spectra