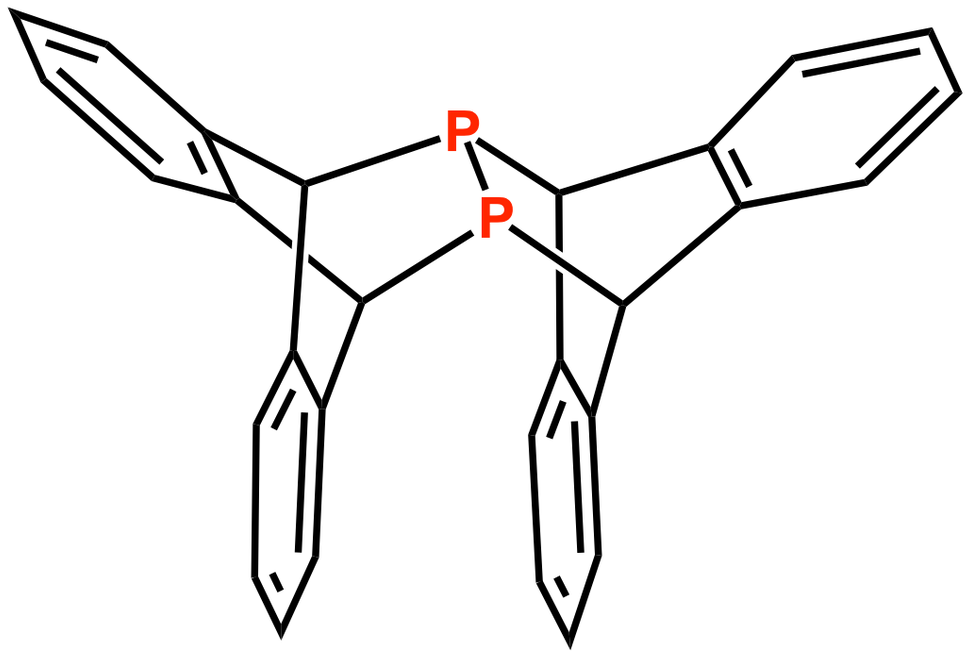
Academic Career Summary

Christopher C. Cummins



Yongliang Zhang

2020.07.08

Christopher C. Cummins

Born Feb. 28th, 1966, Boston

Education

1989 A.B. Chemistry, Cornell University

Advisor: Peter T. Wolczanski

1993 Ph.D. Inorganic Chemistry, MIT

Advisor: Richard R. Schrock

Experience

1993 Assistant Professor, MIT

1996 Professor, MIT

Research interests

Low-coordinated reactive early transition-metal complexes;

Functionalization of metal-element triple bonds;

Activation of small molecules (N_2, P_4, CO_2, CO, O_2, etc.);

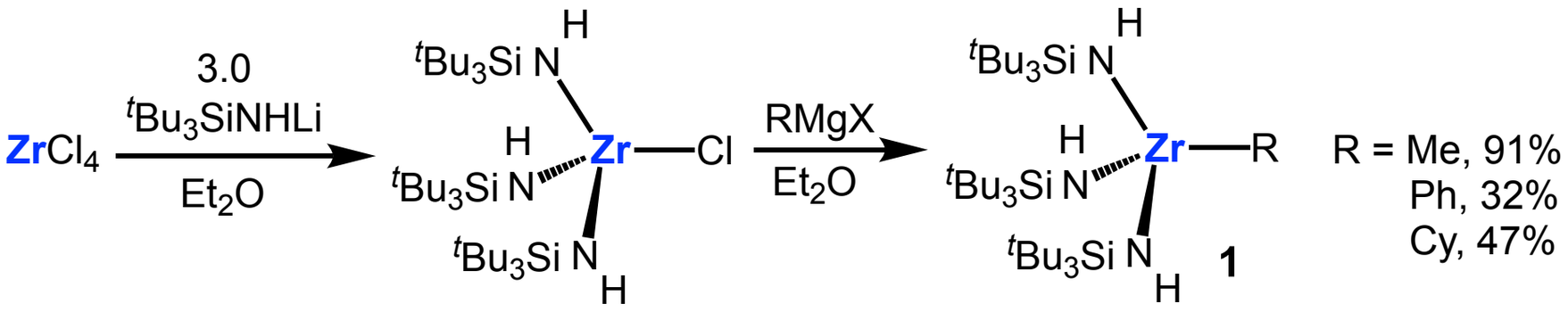
Development of new inorganic functional groups and group transfer reactions;

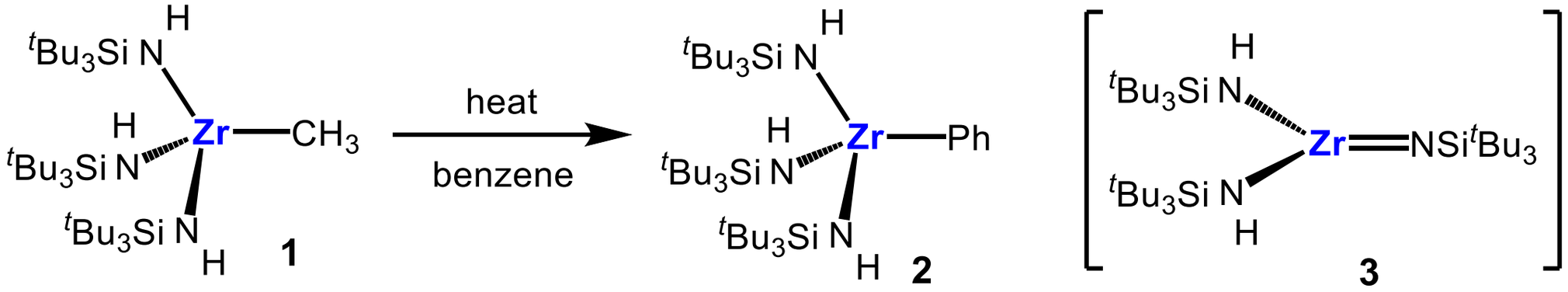
Detailed studies of key reactions.

Outline

- **The work during his A.B. and Ph.D. course**
- Low-coordinated early transition-metal complexes
- Functionalization of metal-element triple bonds
- N_2 activation
- P_4 activation
- Phosphorus-Anthracene (PA) chemistry
- Summary

The work during his A.B. course

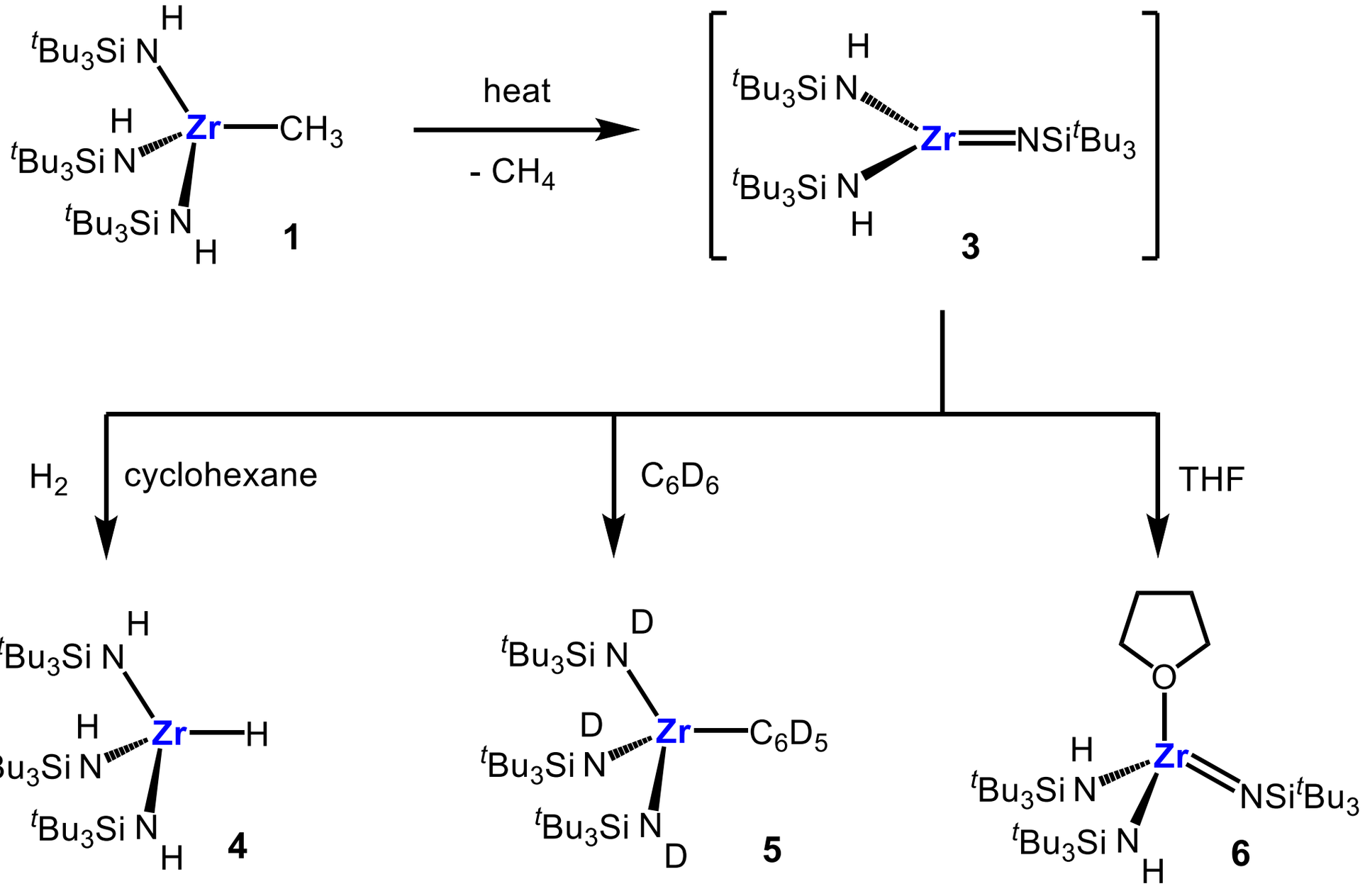




transient zirconium imido species

Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.
Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, E. A.-W.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.
Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczansk. P. T. *Organometallics* **1991**, *10*, 164.

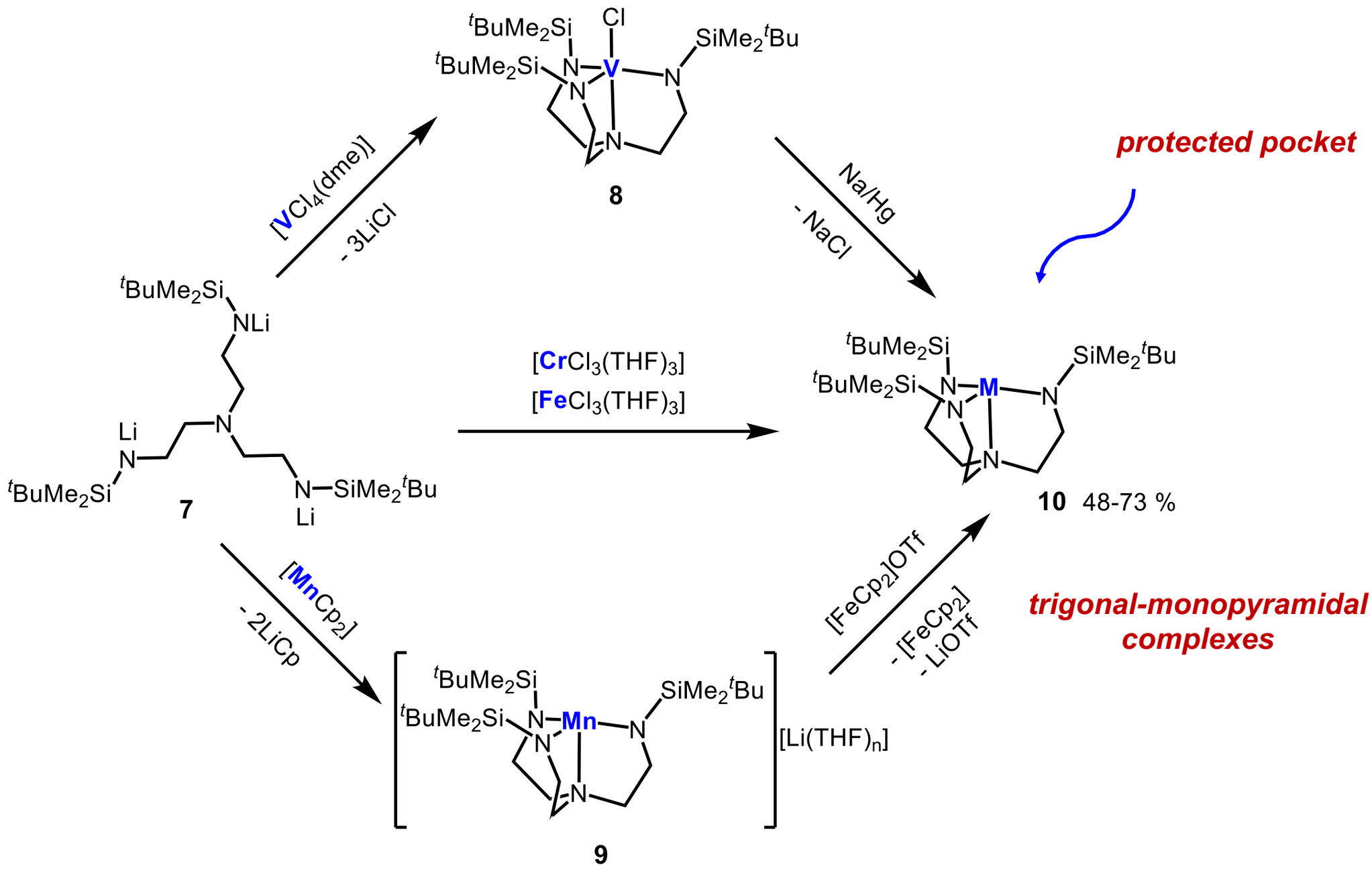
The work during his A.B. course



Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.
Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, E. A.-W.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985.
Cummins, C. C.; Van Duyne, G. D.; Schaller, C. P.; Wolczansk. P. T. *Organometallics* **1991**, *10*, 164.

The work during his Ph.D. course

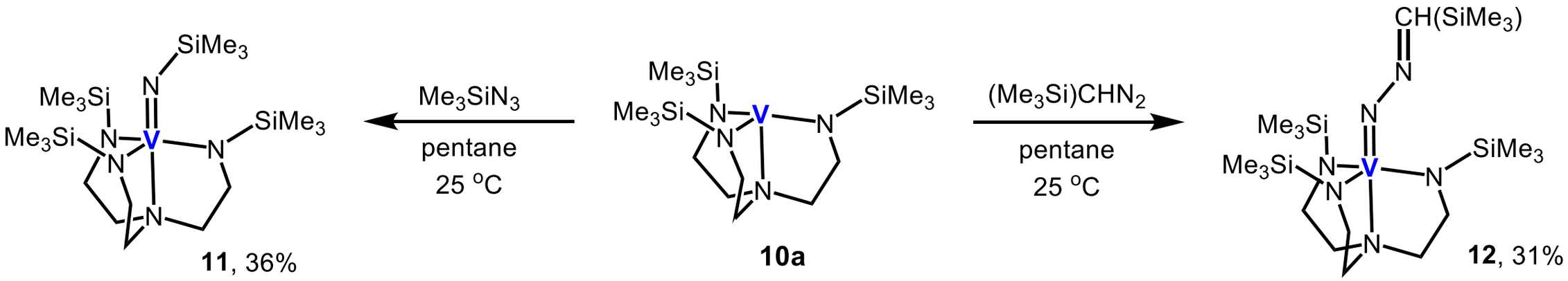
Thesis: Synthetic investigations featuring amidometallic complexes



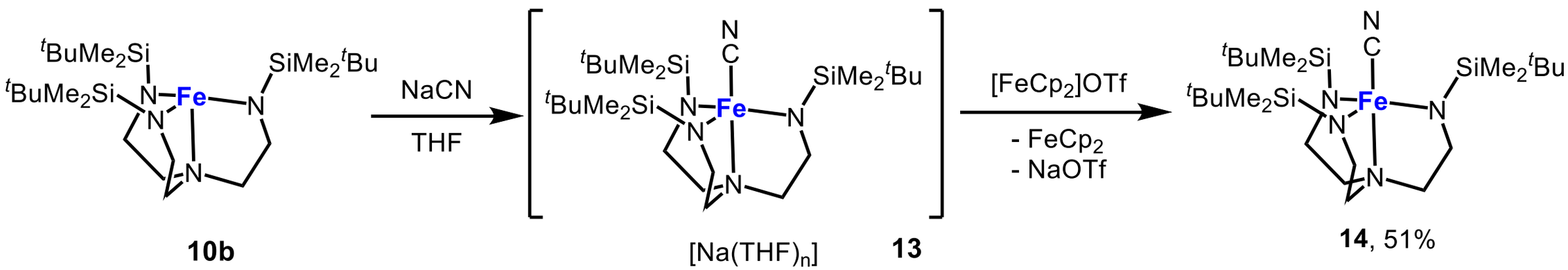
C. C. Cummins, R. R. Schrock, W. M. Davis, *Organometallics* **1992**, *11*, 1452.
Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1501.

The work during his Ph.D. course

Stabilizing the metal imido species



Stabilizing the Fe(IV) species



Curnmins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 756.
Cummins, C. C.; Schrock, R. R.; *Inorg. Chem.* **1994**, *33*, 395.
Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

Outline

- The work during his A.B. and Ph.D. course
- **Low-coordinated early transition-metal complexes**
- Functionalization of metal-element triple bonds
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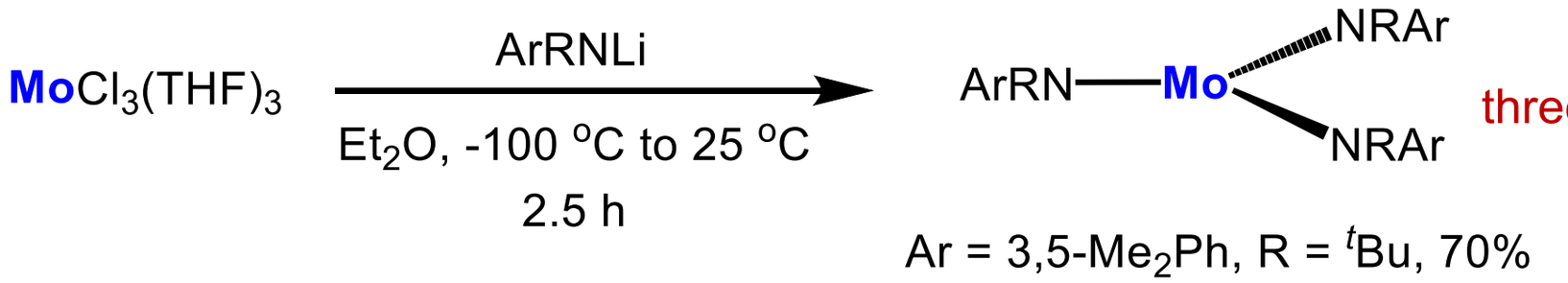
Low-coordinated early transition-metal complexes

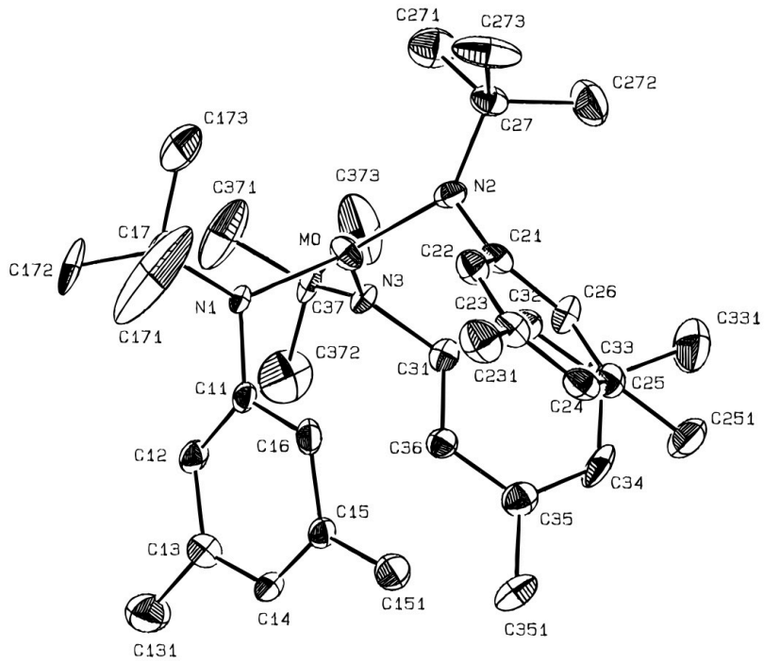


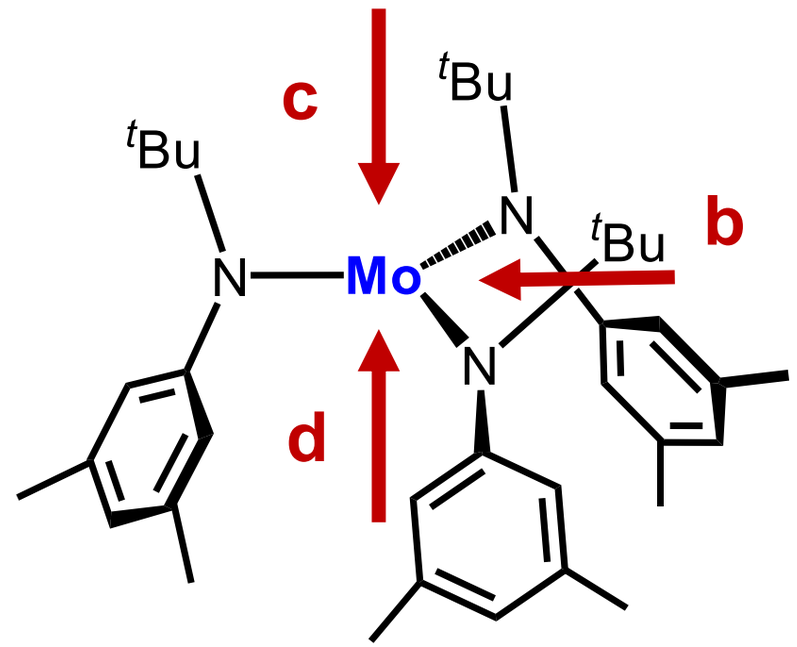
μ_{eff} = 3.56 μ_B

three unpaired electrons

strong π donor

Ar = 3,5-Me_2Ph, R = ^{t}Bu, 70%





(i) a trigonal planar MoN3 unit

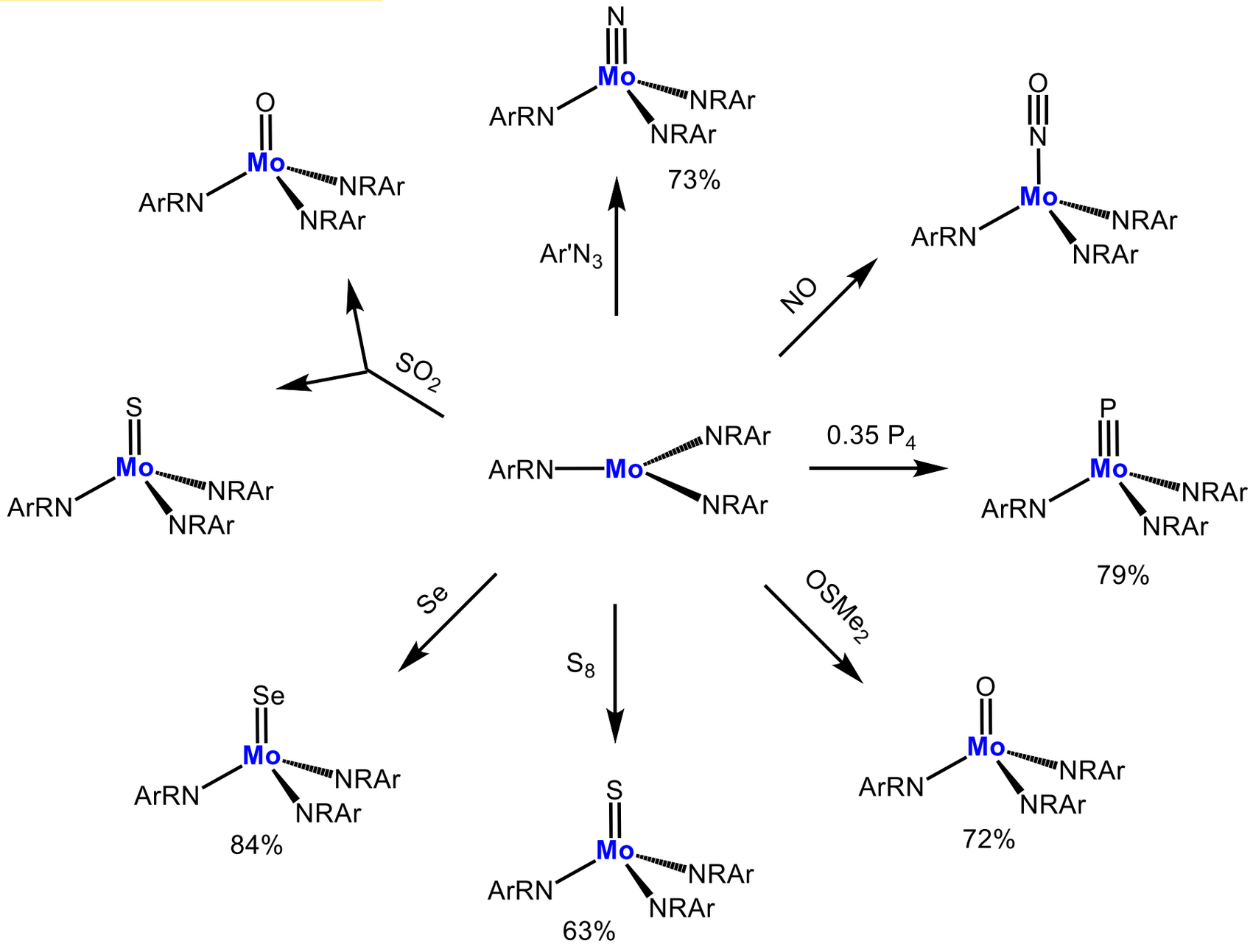
(ii) amido NC2 planes roughly perpendicular to the MoN3 plane

(iii) tert-butyl groups occupying one hemisphere and aryl groups the other

Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 4999.
Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

Low-coordinated early transition-metal complexes

Activation of small molecules



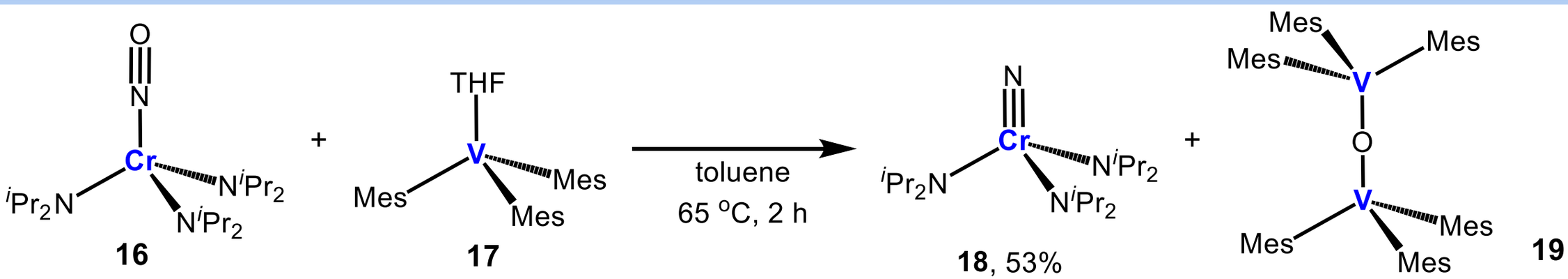
Johnson, A. R.; Davis, W. M.; Cummins, C. C.; Serron, S.; Nolan, S. P. Musaev, D. J.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 2071.

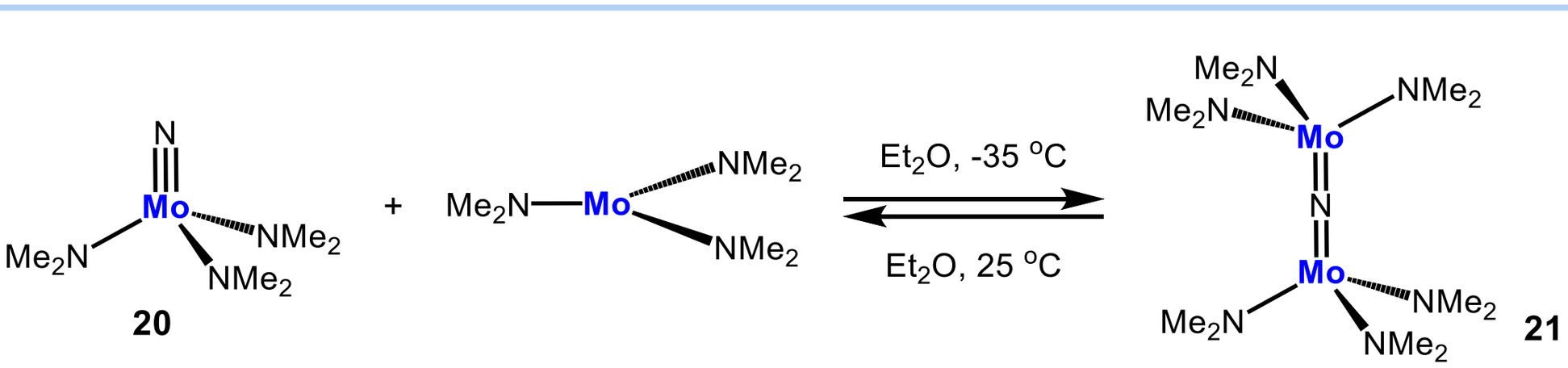
Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 4999.

Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew Chem. Int. Ed. Engl.* **1995**, *34*, 2042.

Low-coordinated early transition-metal complexes

Group transfer reactions



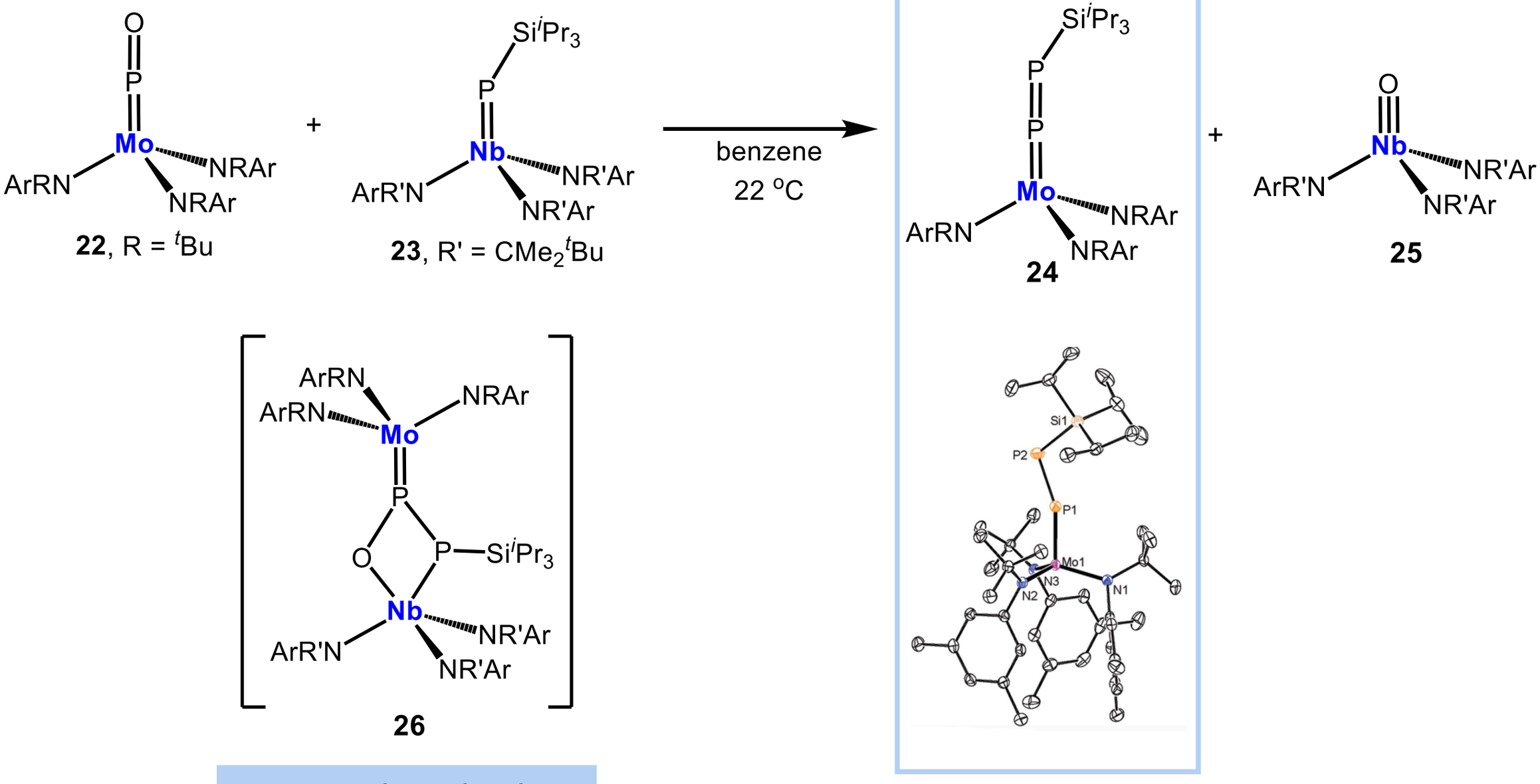


bimetallic species as intermediate

Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613.
Johnson, M. J. A.; Lee, P. M.; Odom, A. L.; Davis, W. M.; Cummins, C. C. *Angew Chem. Int. Ed. Engl.* **1997**, *36*, 87.

Low-coordinated early transition-metal complexes

Group transfer reactions



concerted mechanism
oxyphilic property

Piro, N. A.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 8764.

Outline

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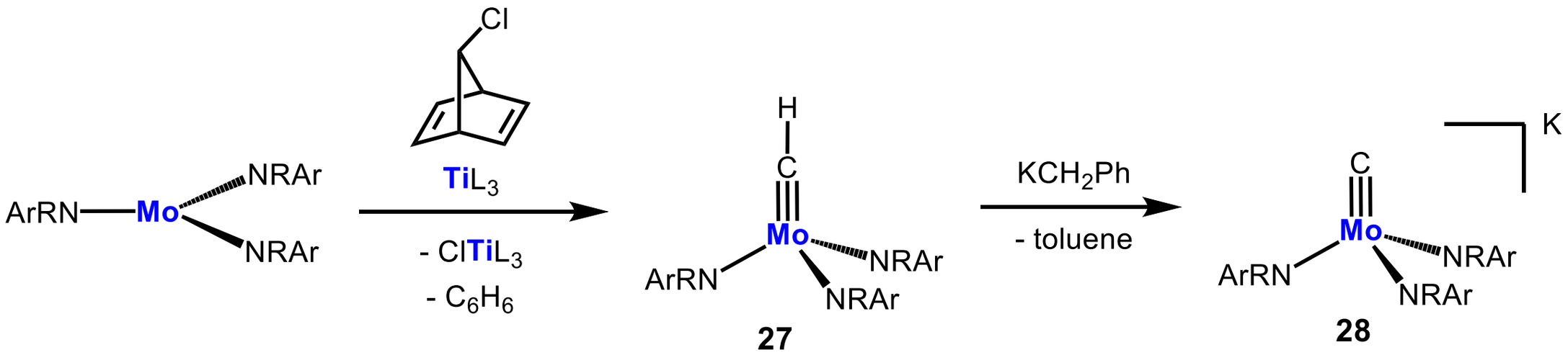
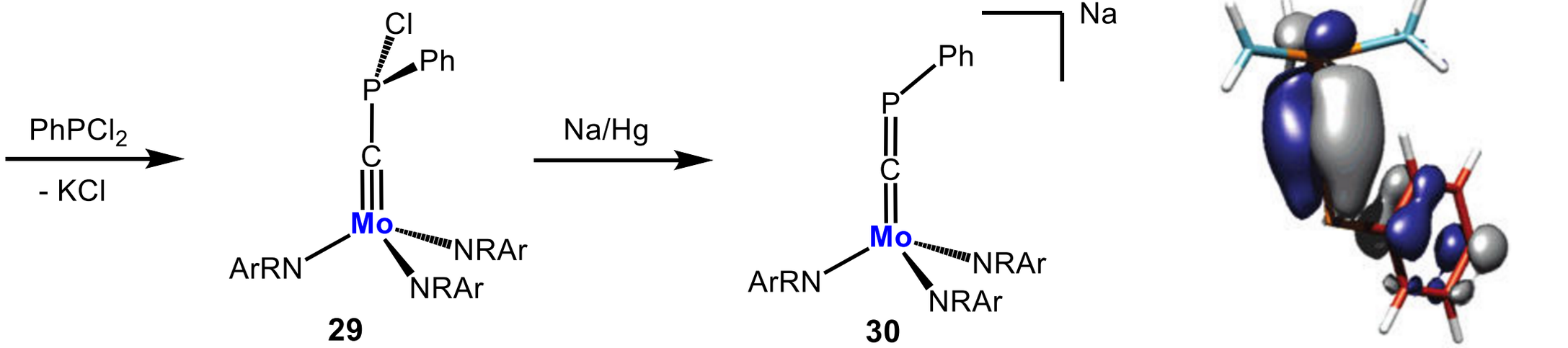
Functionalization of metal-element triple bonds

Carbide early transition-metal complexes





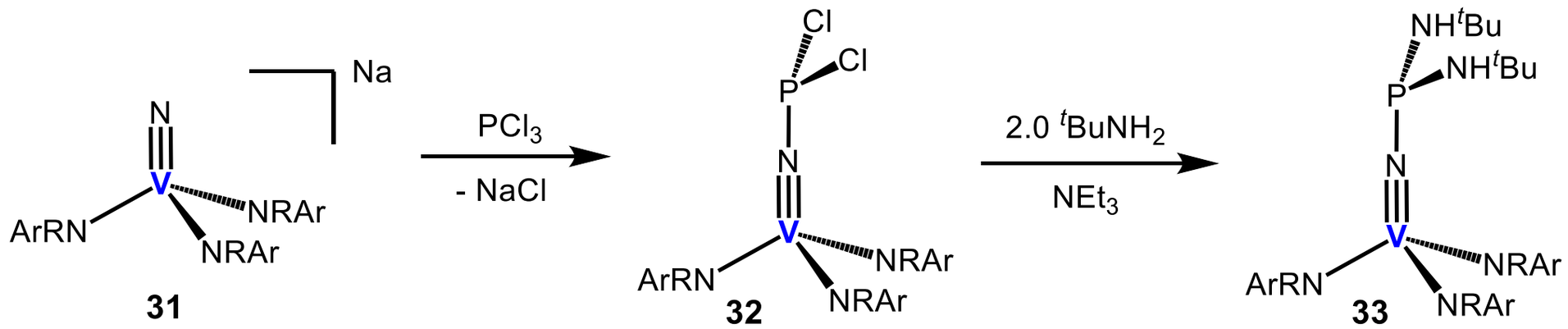
metal stabilized phosphene species

π bonding interaction between Mo, C, and P atoms

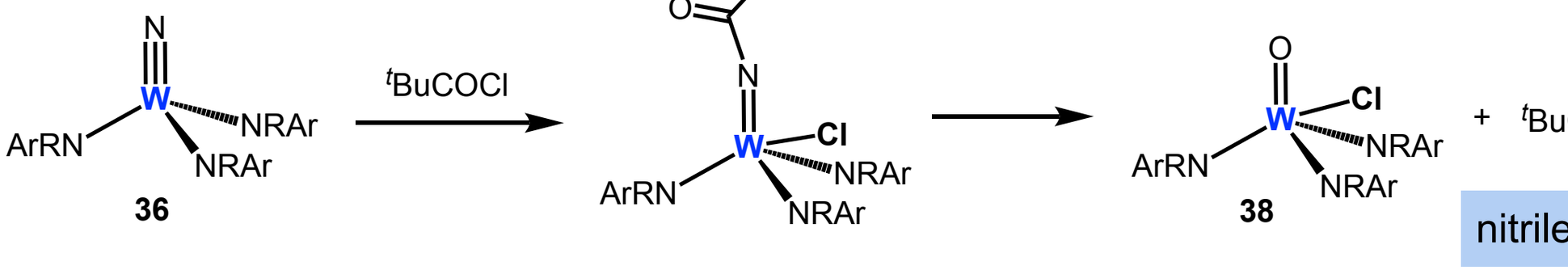
Agapie, T.; Diaconescu, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 2412.
Cummins, C. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 862.

Functionalization of metal-element triple bonds

Nitride early transition-metal complexes



P=N precursors

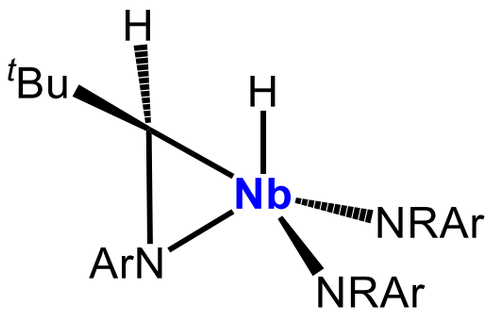


nitriles from N_2

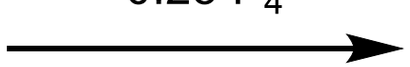
Brask, J. K.; Fickes, M. G.; Sangtrirutnugul, P.; Durà-Vilà, V.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **2001**, 1676.
Clough, C. R.; Greco, J. B.; Figueroa, J. S.; Diaconescu, P. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 7742.
Cummins, C. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 862.

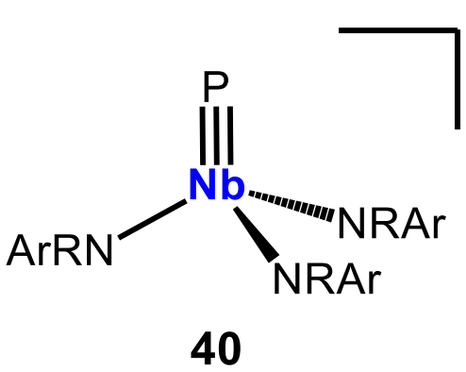
Functionalization of metal-element triple bonds

Phosphide early transition-metal complexes



39, R = $CH_2{}^tBu$





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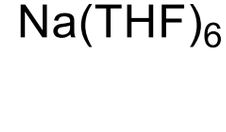

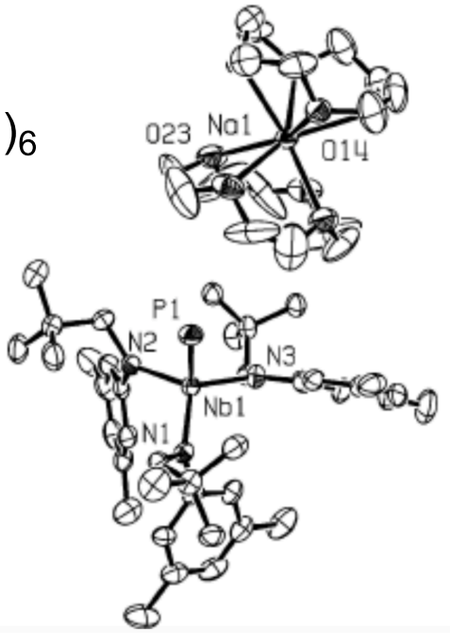

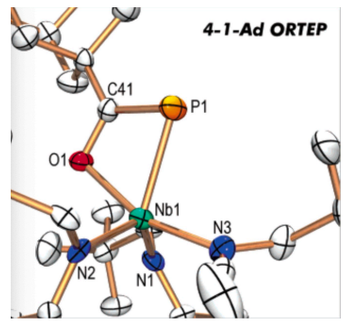

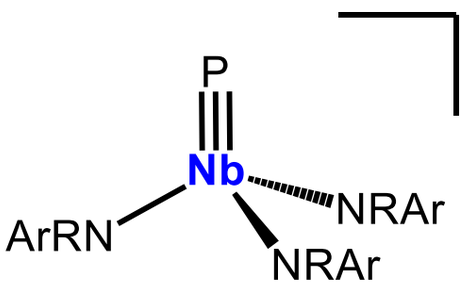

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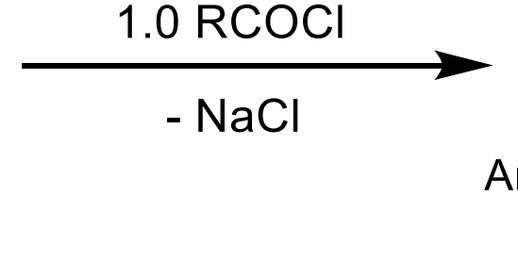

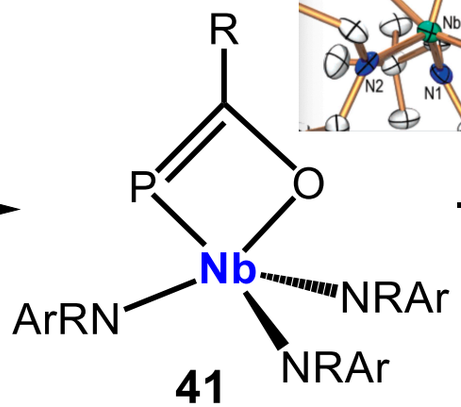

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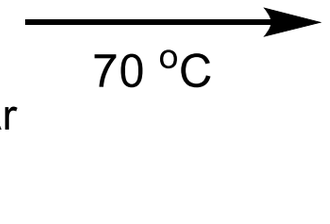

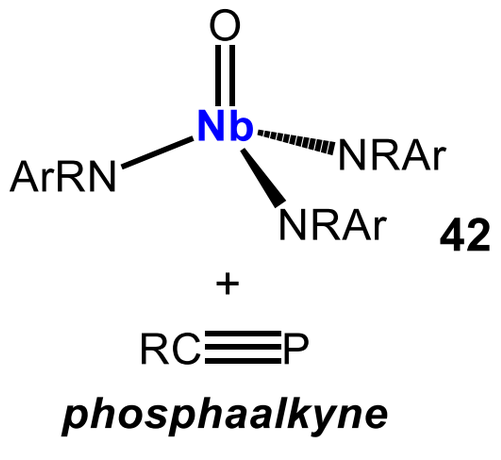

phosphaalkyne

phosphaalkyne from P_4

Figueroa, J. S.; Cummins. C. C. *J. Am. Chem. Soc.* **2003**, *125*, 4020.
Figueroa, J. S.; Cummins. C. C. *Angew. Chem. Int. Ed*. **2004**, *43*, 984.
Figueroa, J. S.; Cummins. C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916.

Outline

- The work during his A.B. and Ph.D. course
- Low-coordinated early transition-metal complexes
- Functionalization of metal-element triple bonds
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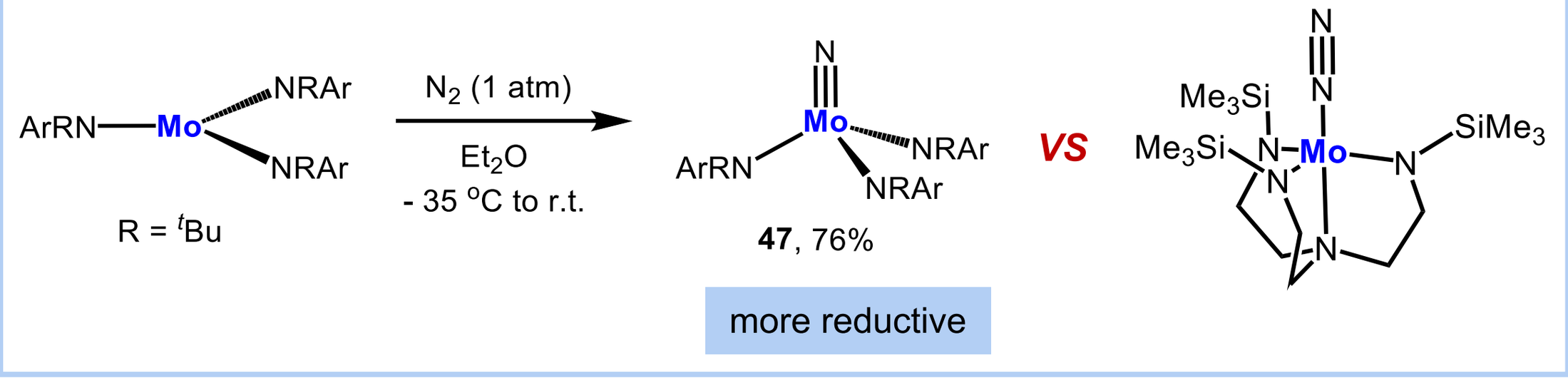
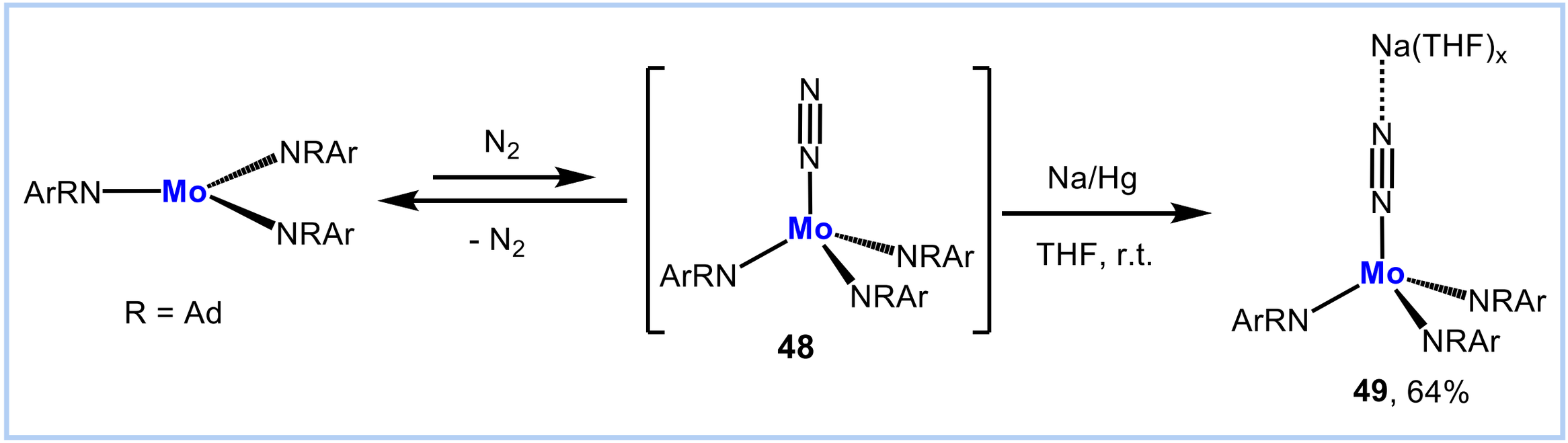
N_2 activation

Reaction of MoL_3 with N_2



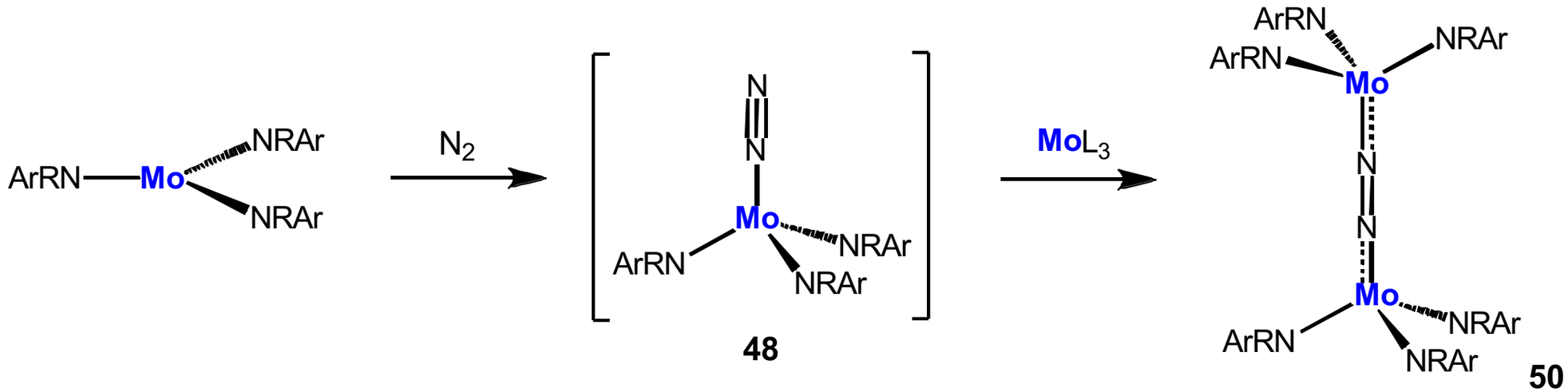


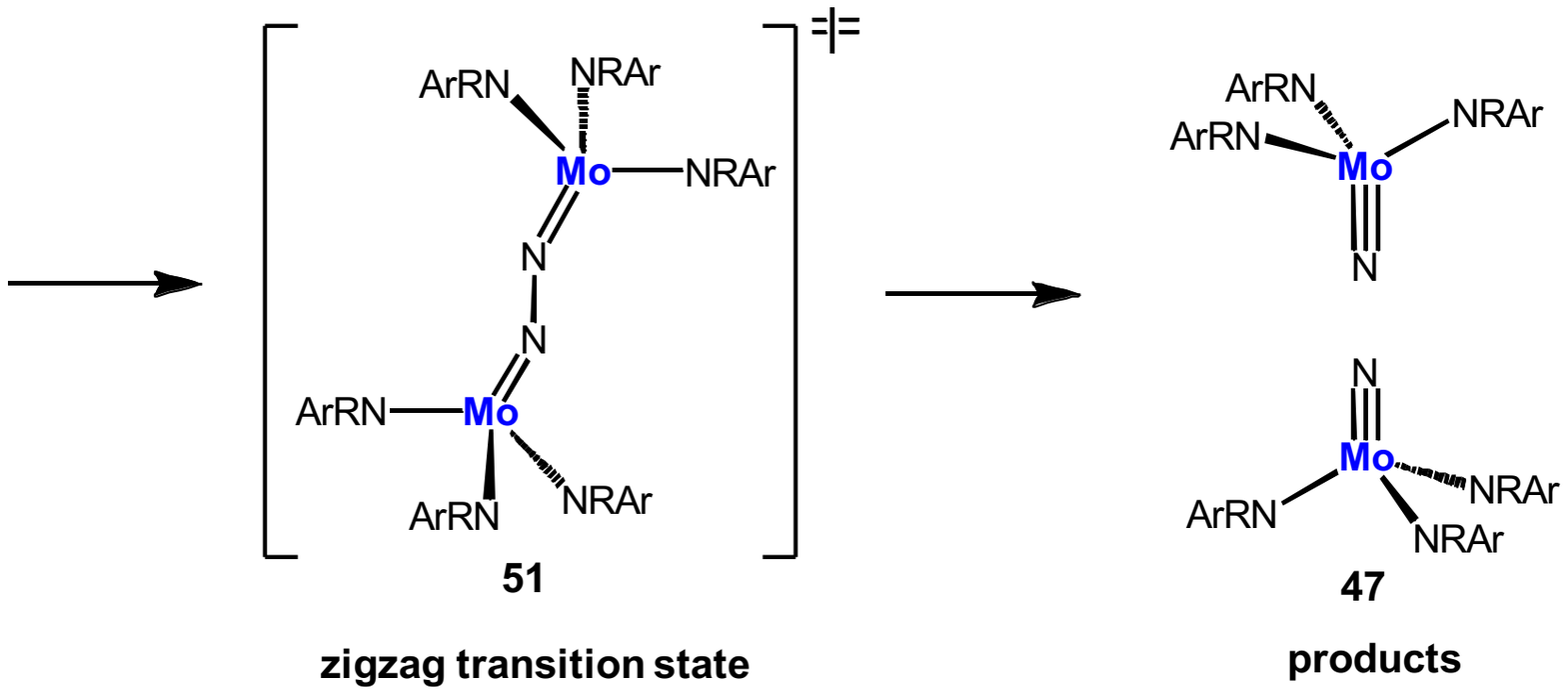
Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. D.; Cummins, C. C. *J. Am. Chem. Soc.* **1999**, *121*, 10053.

N_2 activation

Proposed mechanism



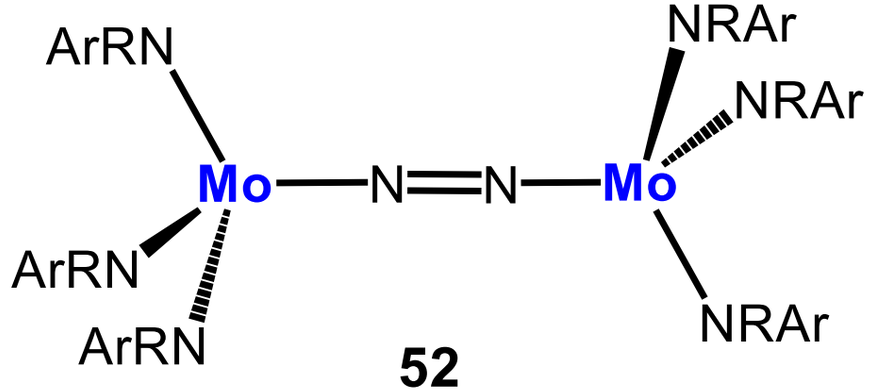


bimetallic species as intermediate

Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623.

N_2 activation

Bimetallic intermediate



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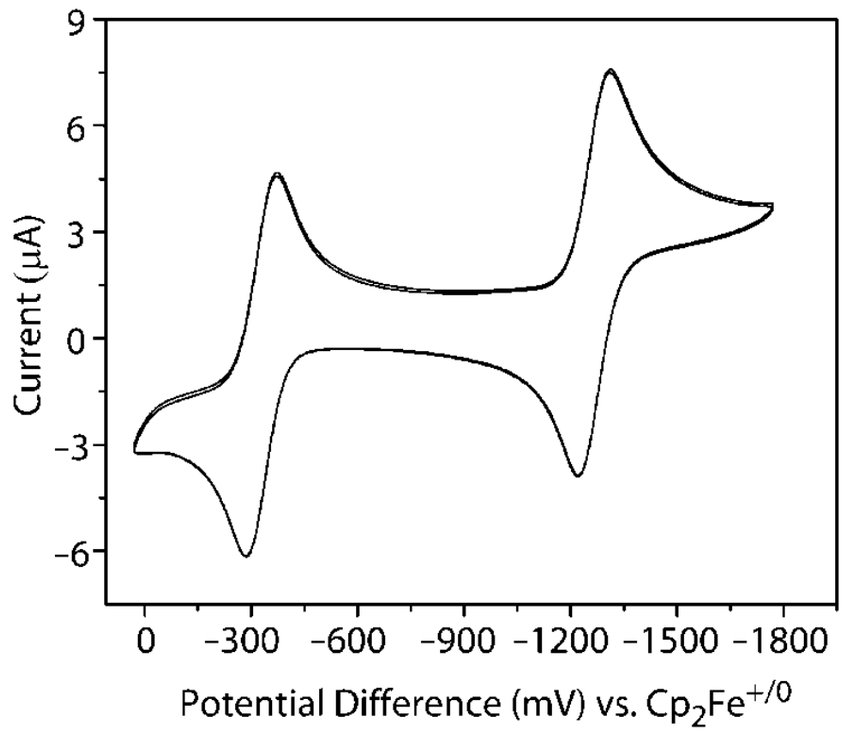
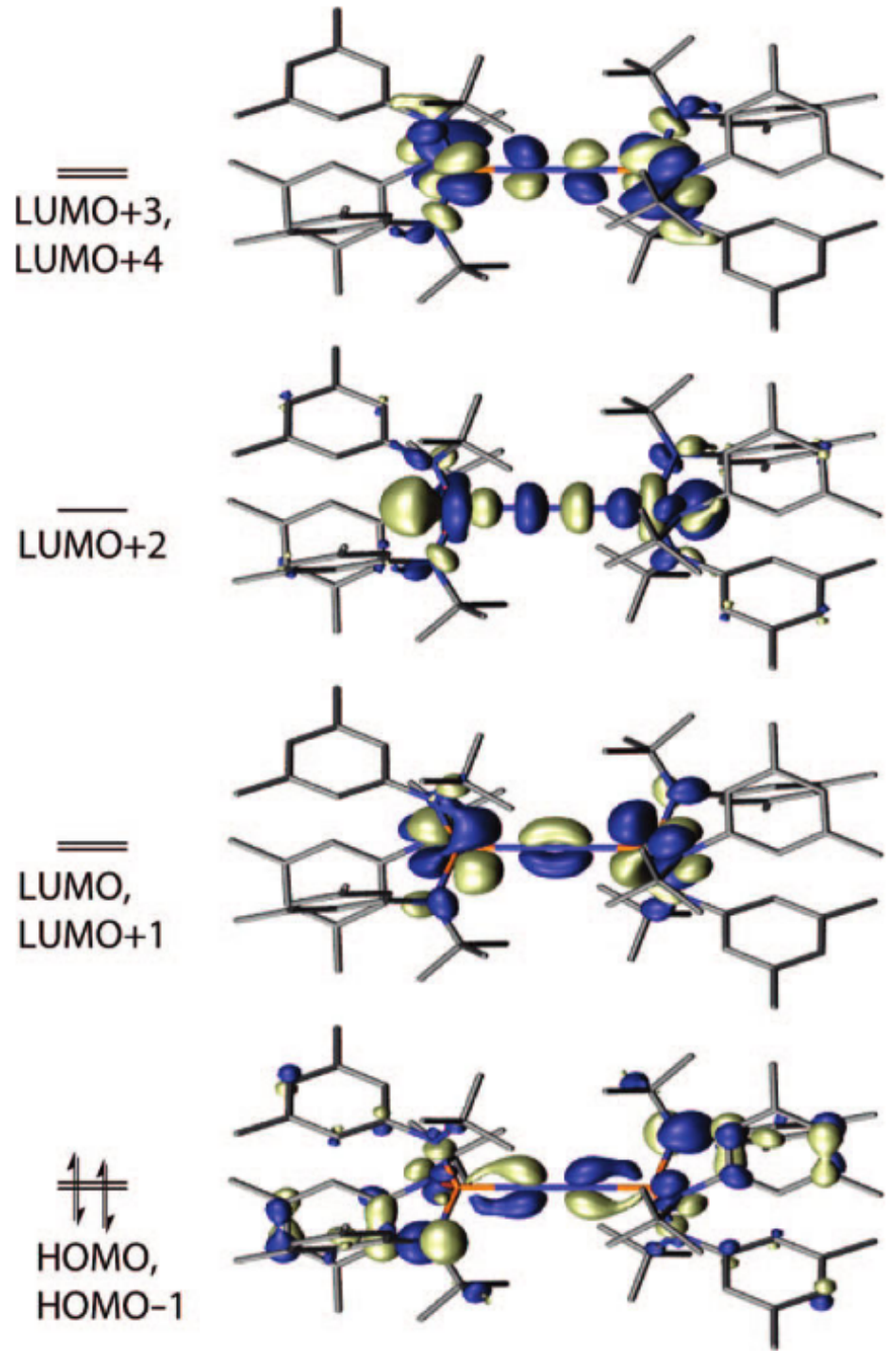


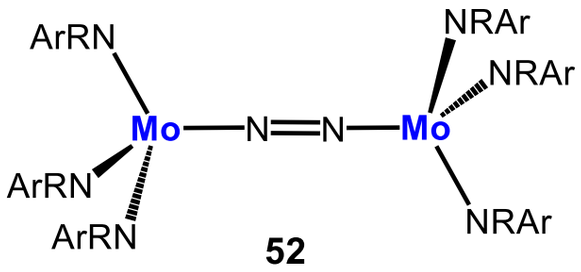


Curley, J. J.; Cook, T. R.; Reece, S. Y.; Müller, P.; Cummins, C. C. *J. Am. Chem. Soc.* **2008**, *130*, 9394.

N_2 activation

Bimetallic intermediate

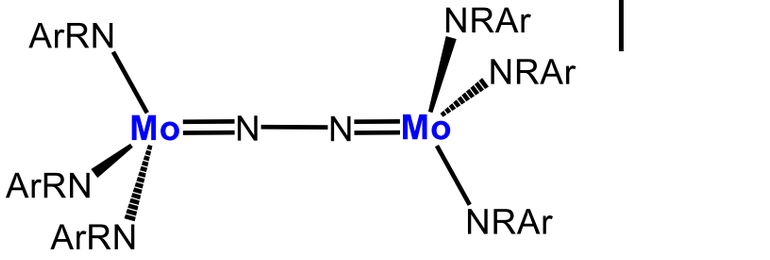
1.212(2) Å
1630 cm^{-1}



52

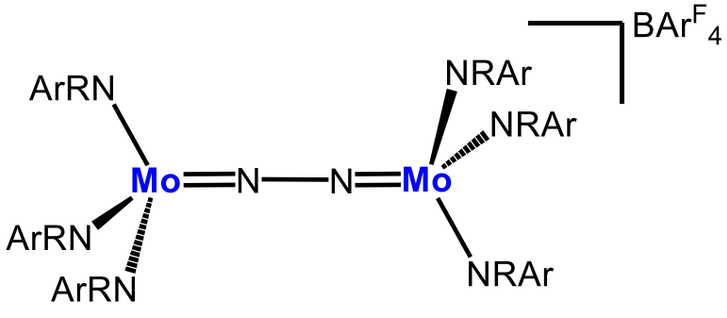
2 [FeCp$_2$] [BAr$^F{}_4$] ⇄ K_2COT

1.239(4) Å
1503 cm^{-1}

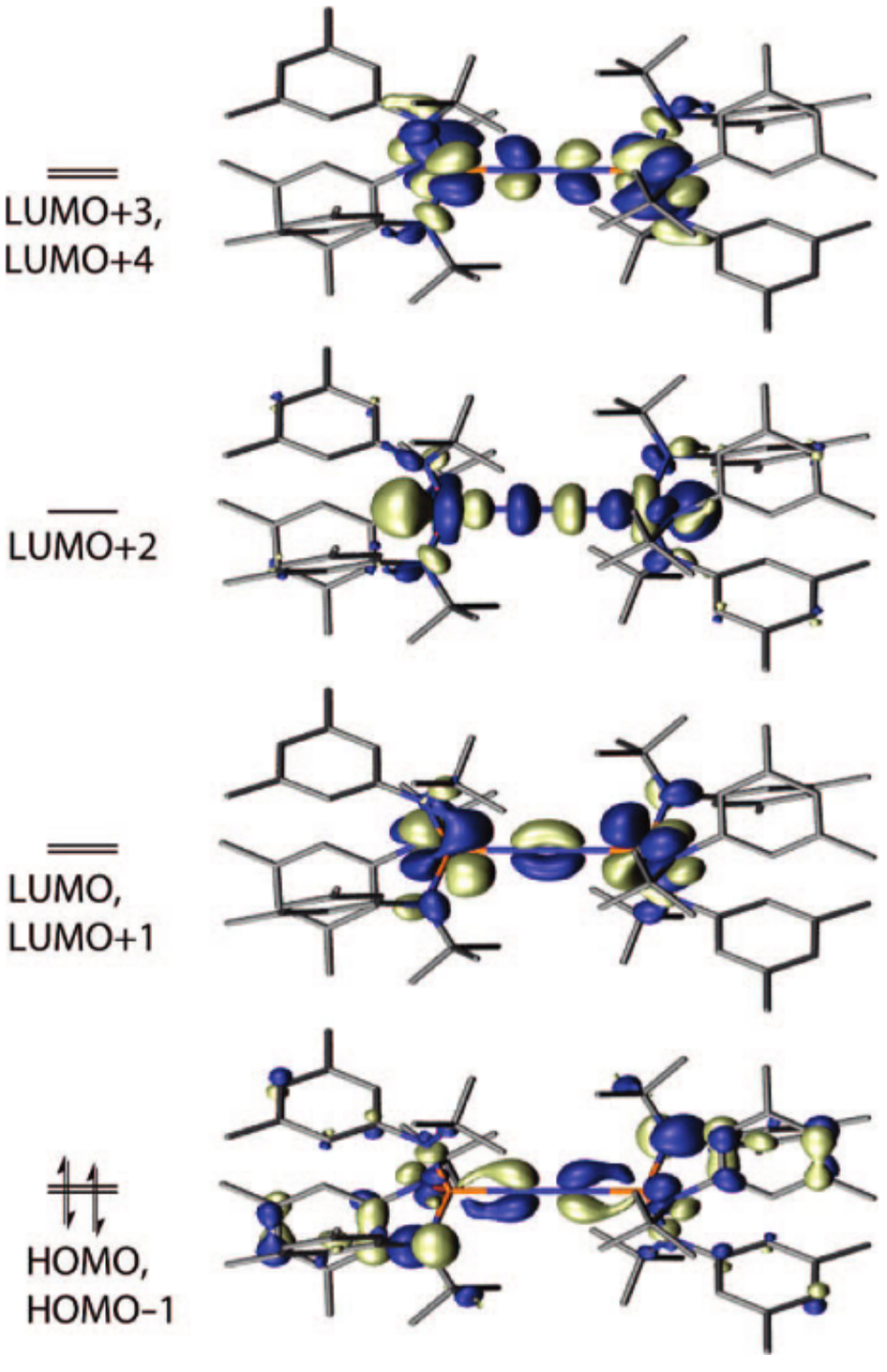


53, 98%

1.265(5) Å
1349 cm^{-1}



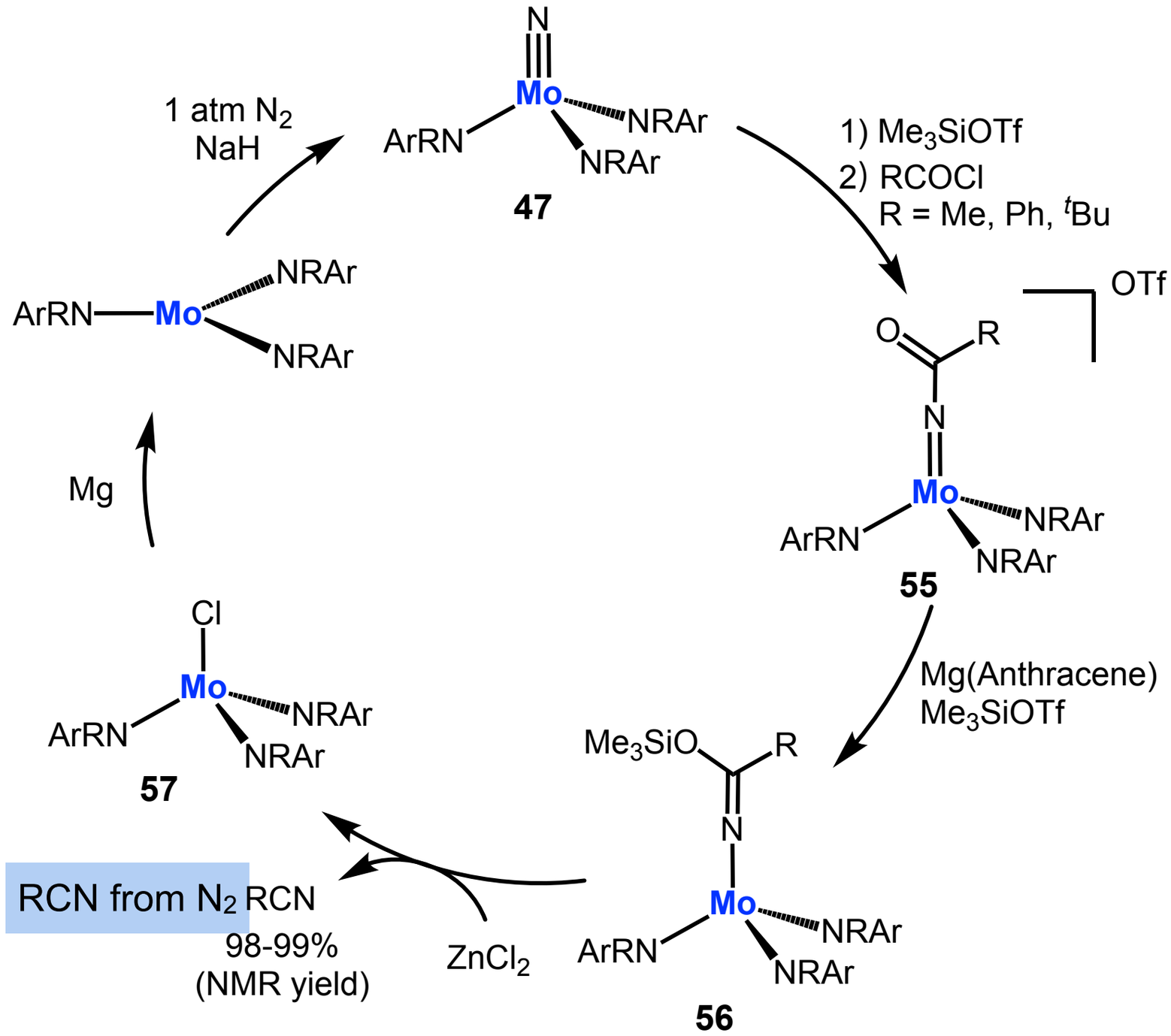
54, 95%



Curley, J. J.; Cook, T. R.; Reece, S. Y.; Müller, P.; Cummins, C. C. *J. Am. Chem. Soc.* **2008**, *130*, 9394.

N_2 activation

Synthetic cycle



Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036.

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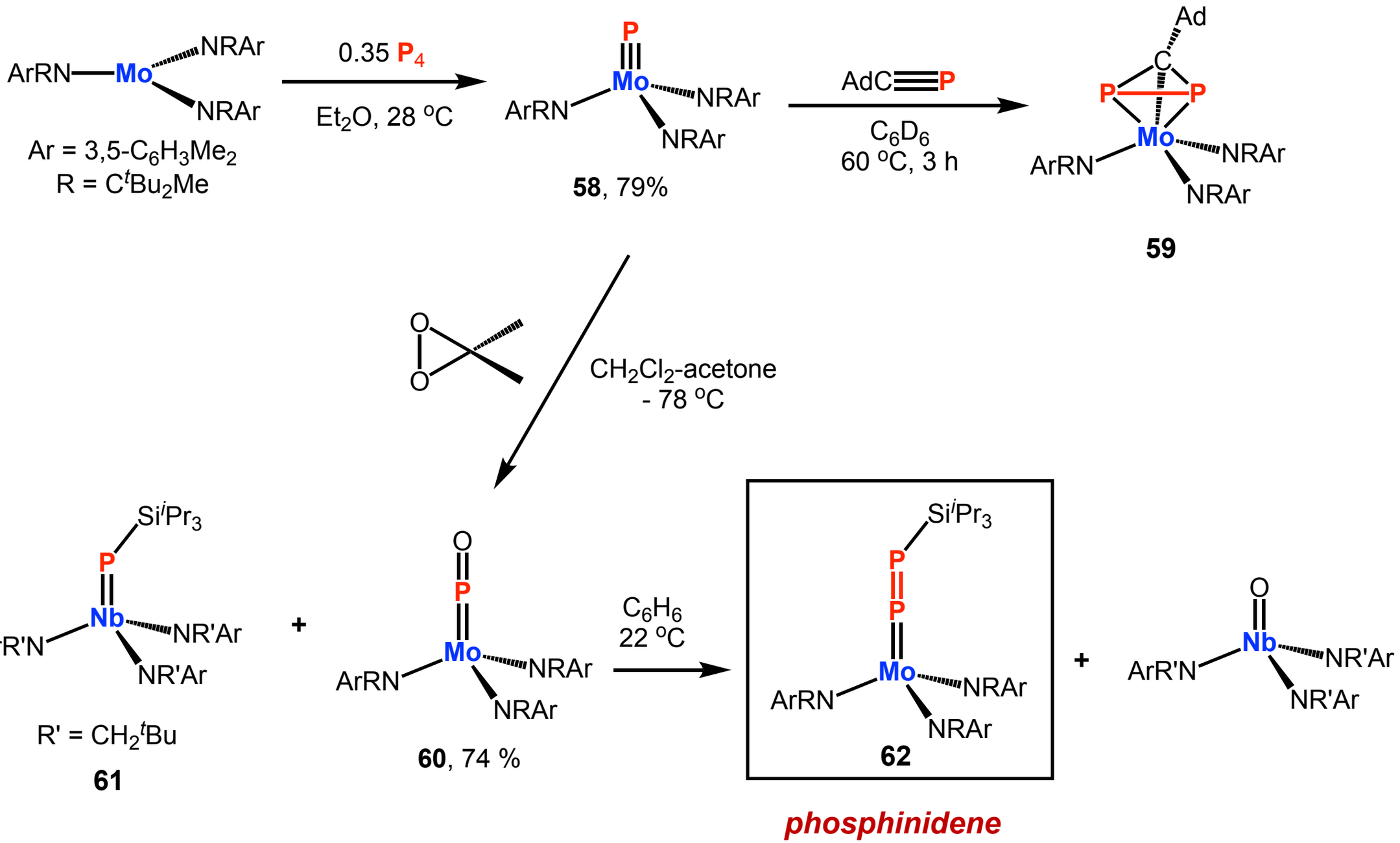
P_4 activation



Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2042.
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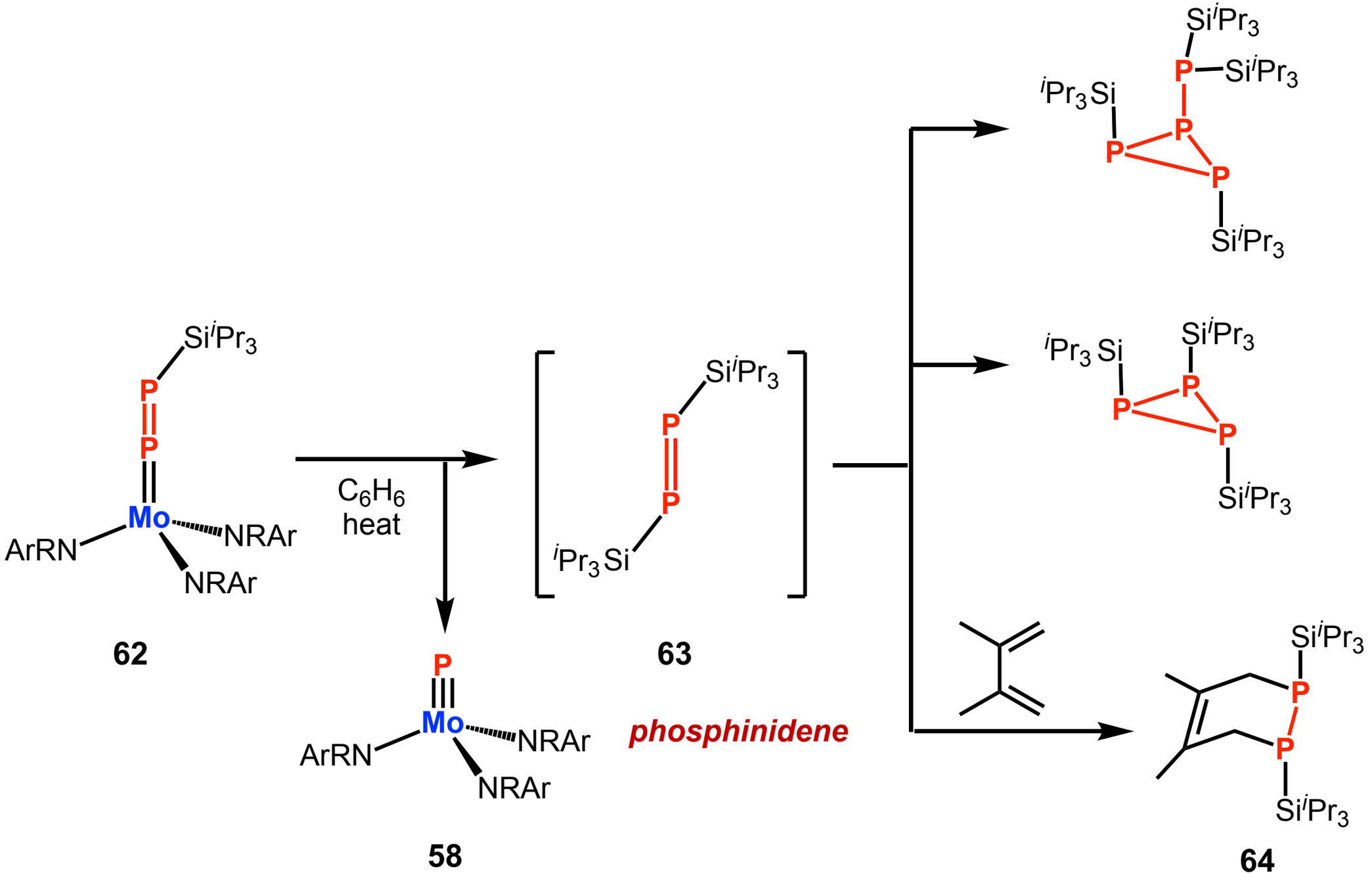
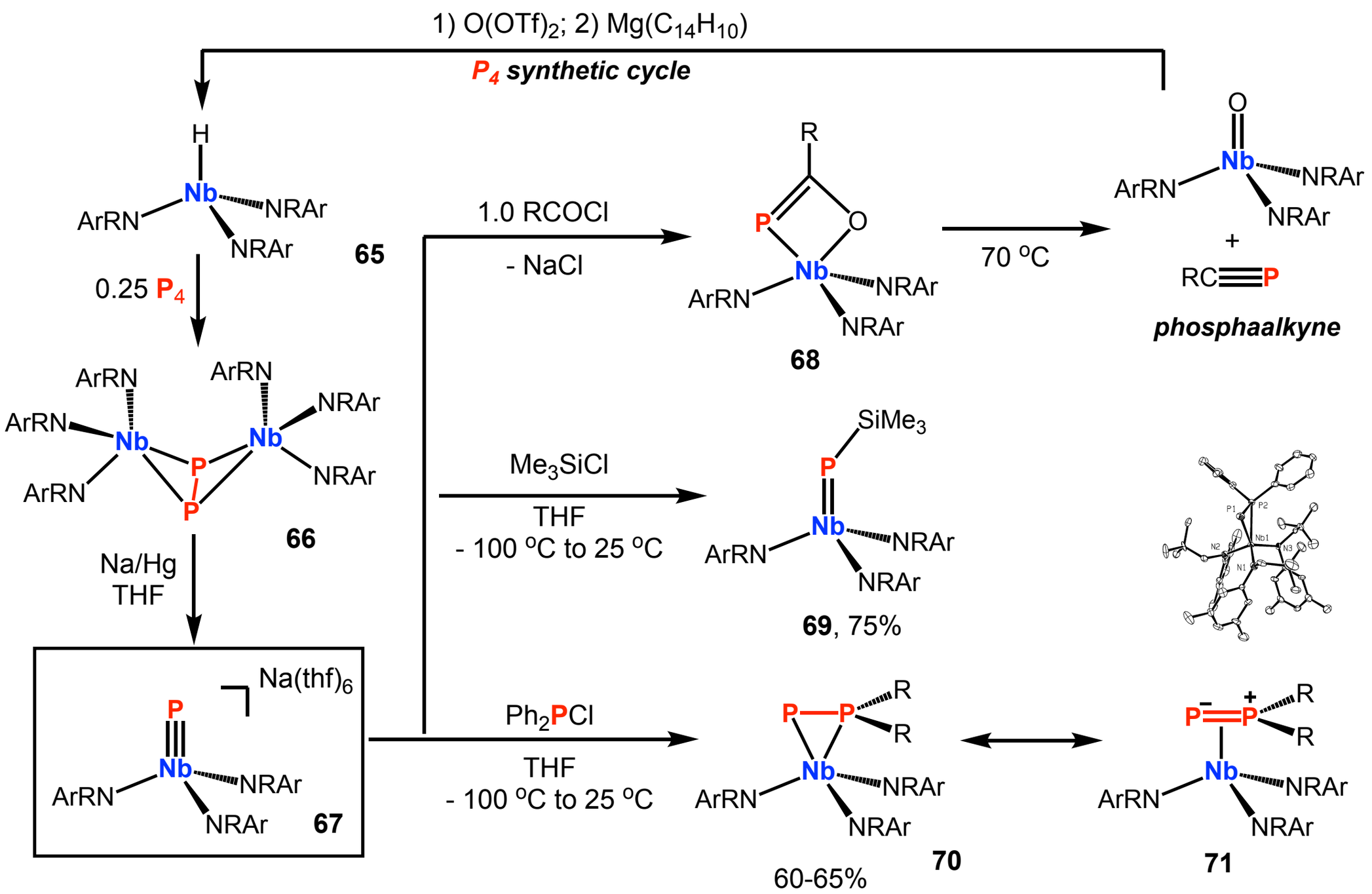
Piro, N. A.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 8764.

P_4 activation



Piro, N. A.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 8764.

P_4 activation



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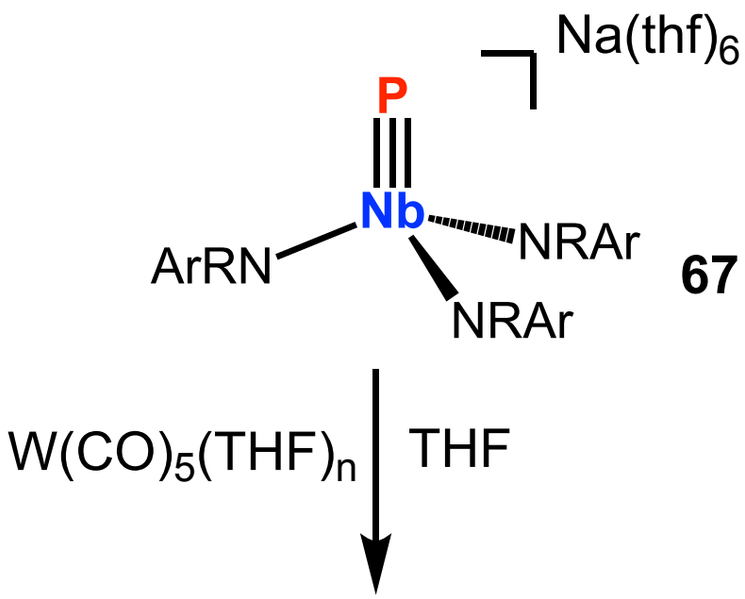
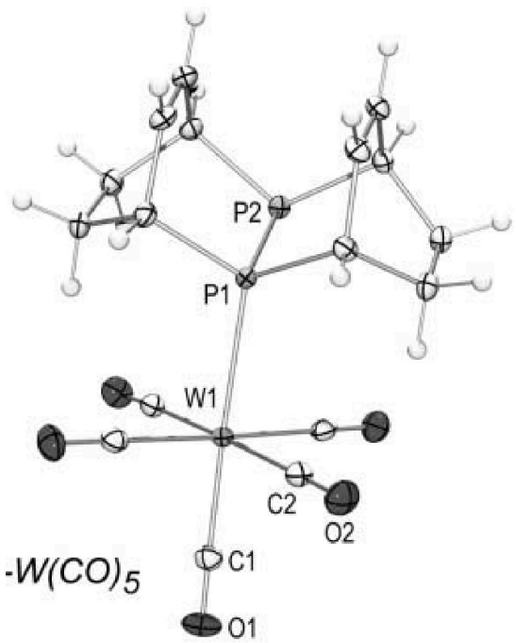
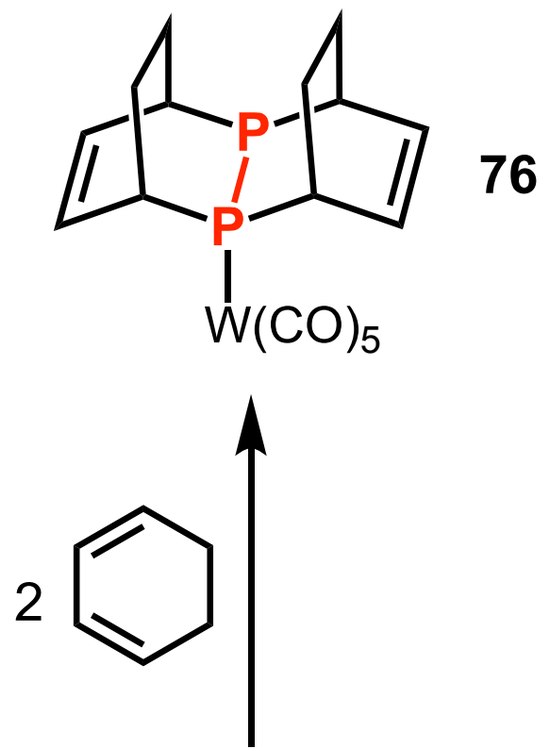
Figueroa, J. S.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 984.
Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916.

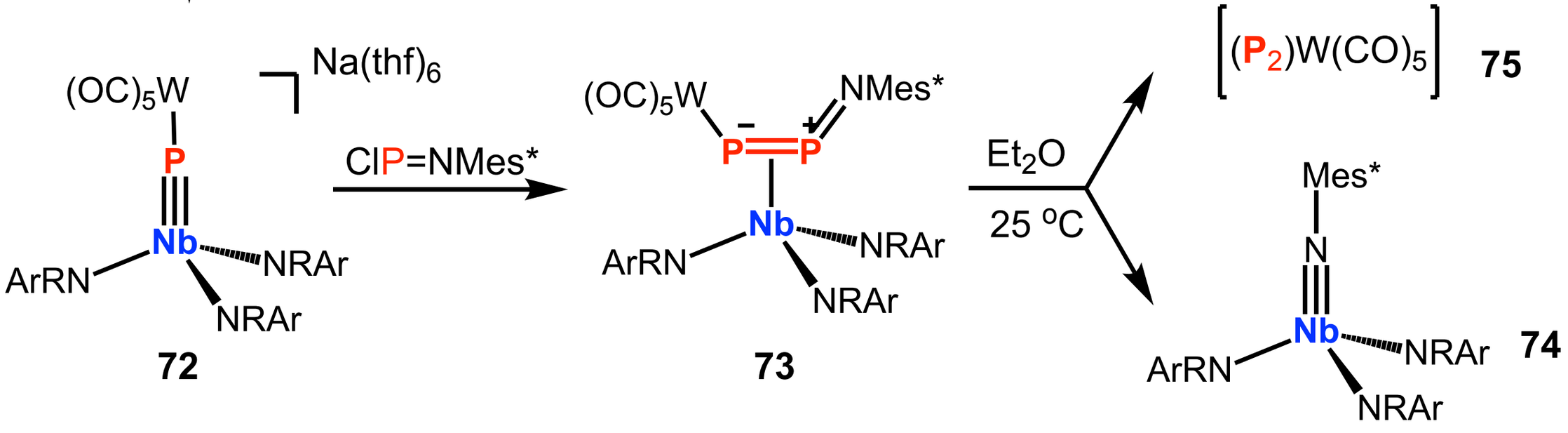
P_4 activation

Triple-bond reactivity of diphosphorus molecules









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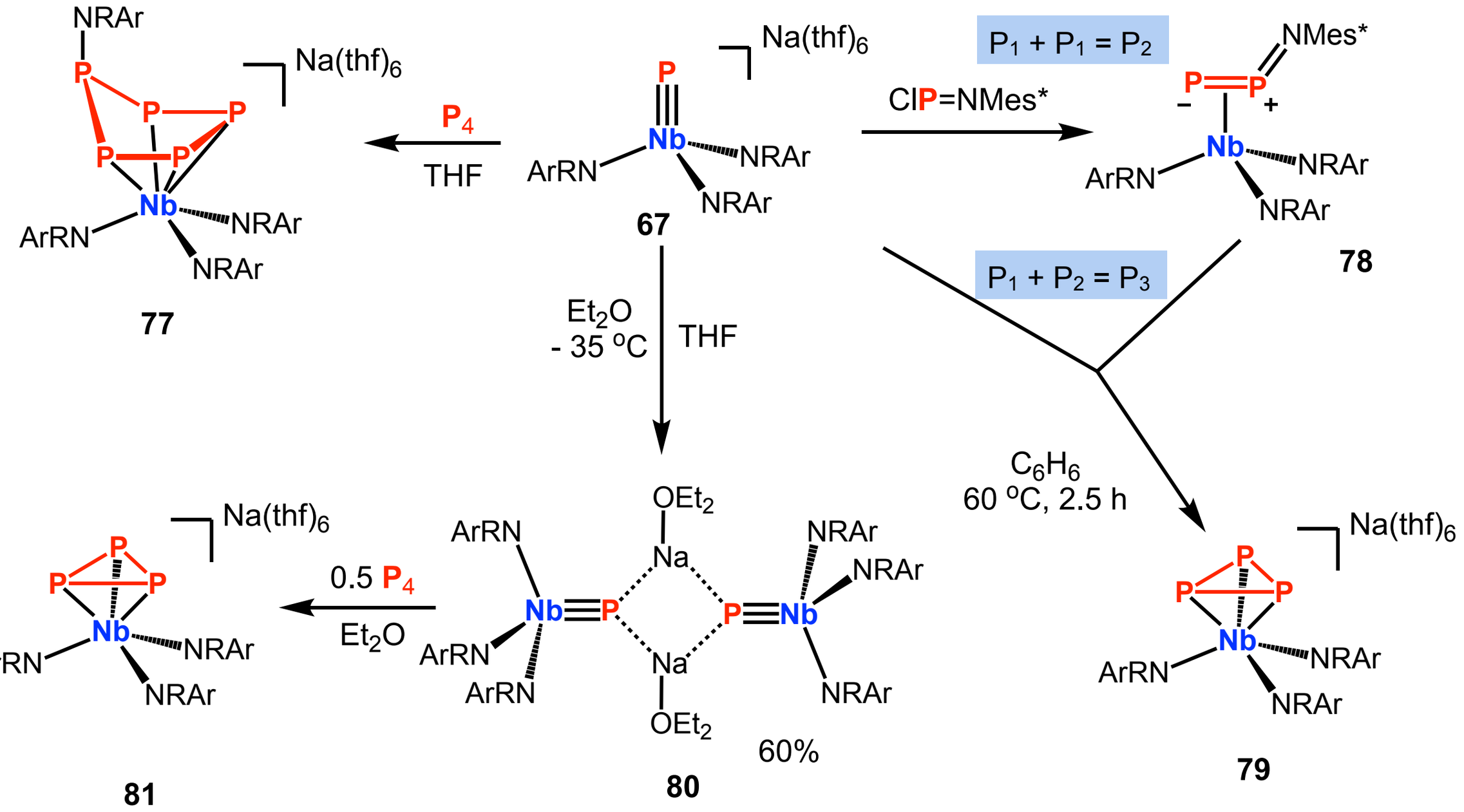
Tofan, D.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2010**, *49*, 7516.

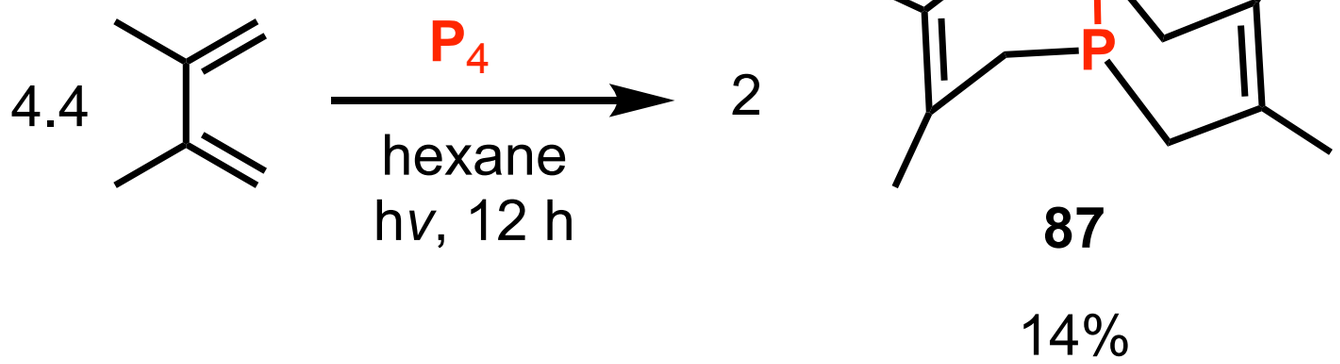
P_4 activation

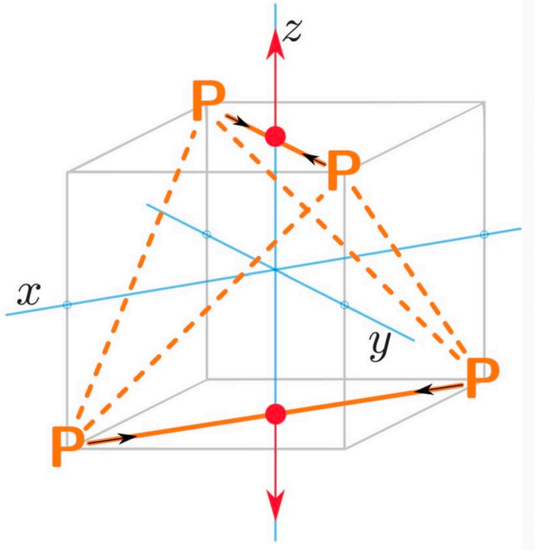


Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 4020;
Figueroa, J. S.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 984;
Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916;

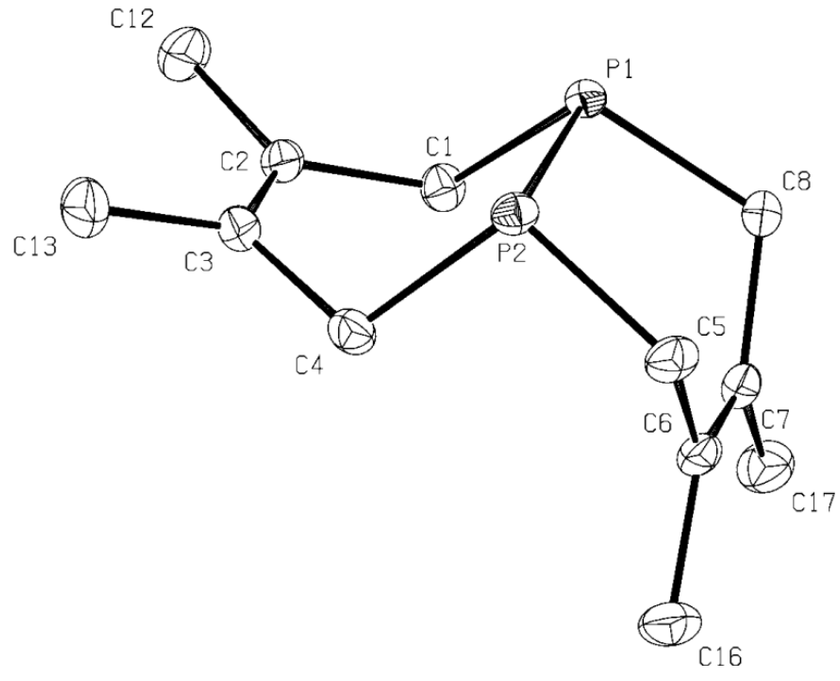
P_4 activation

Photolytic activation of P_4





simultaneous
breaking of four P–P bonds



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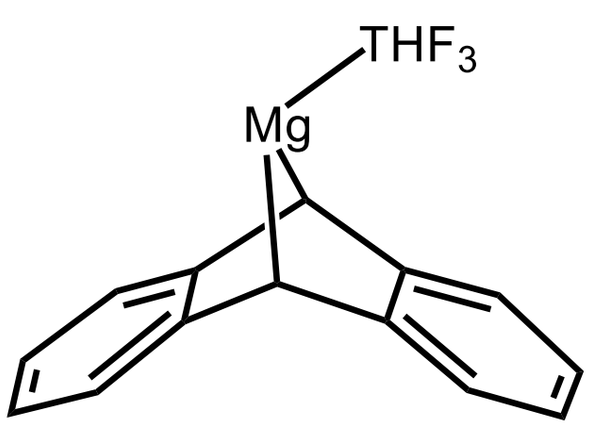
Outline

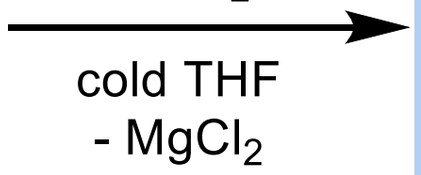
- The work during his A.B. and Ph.D. course
- Low-coordinated early transition-metal complexes
- Functionalization of metal-element triple bonds
- N_2 activation
- P_4 activation
- **Phosphorus-Anthracene (PA) chemistry**
- Summary

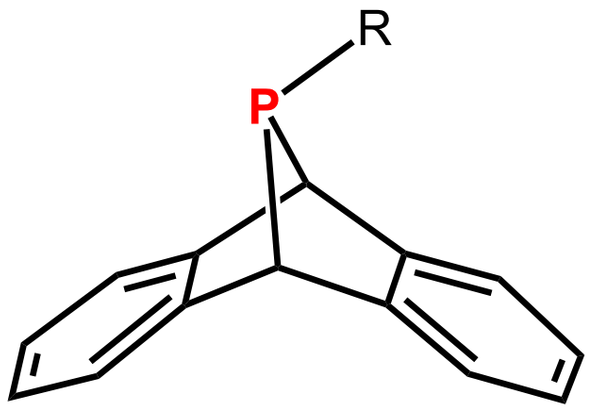
PA chemistry

Synthesis of RPA and phosphinidene



88

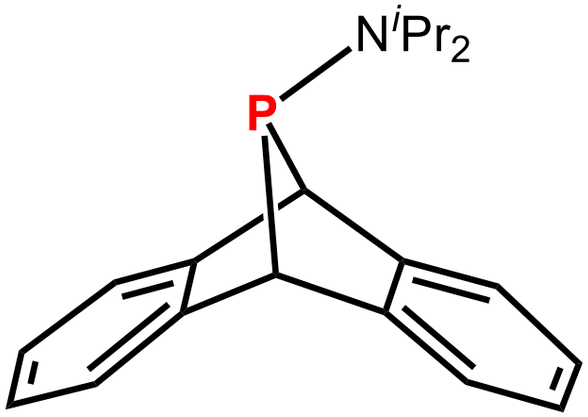




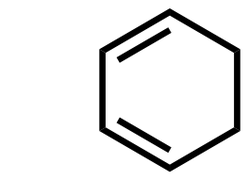
89, R = ^{t}Bu, N(SiMe$_3$)$_2$, N^{i}Pr$_2$

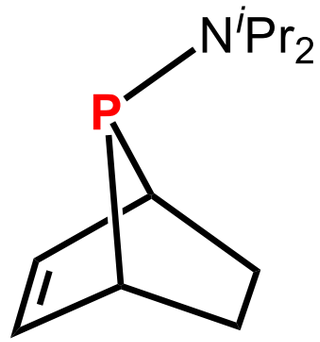
20-30 %

unprotected lone pair
high strain (79º)
P1 precursors

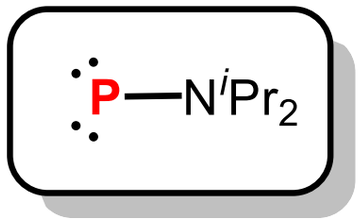


89a





90, 69%



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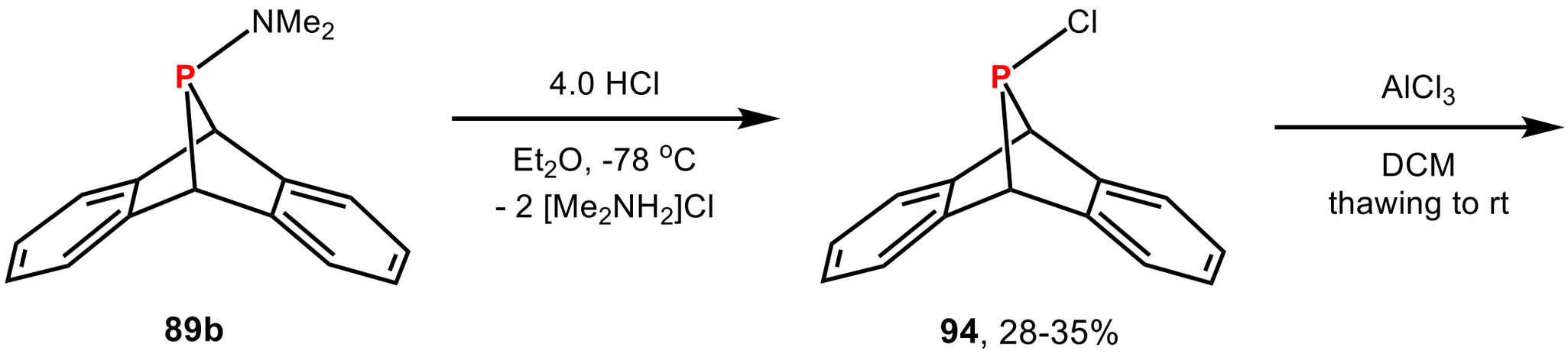
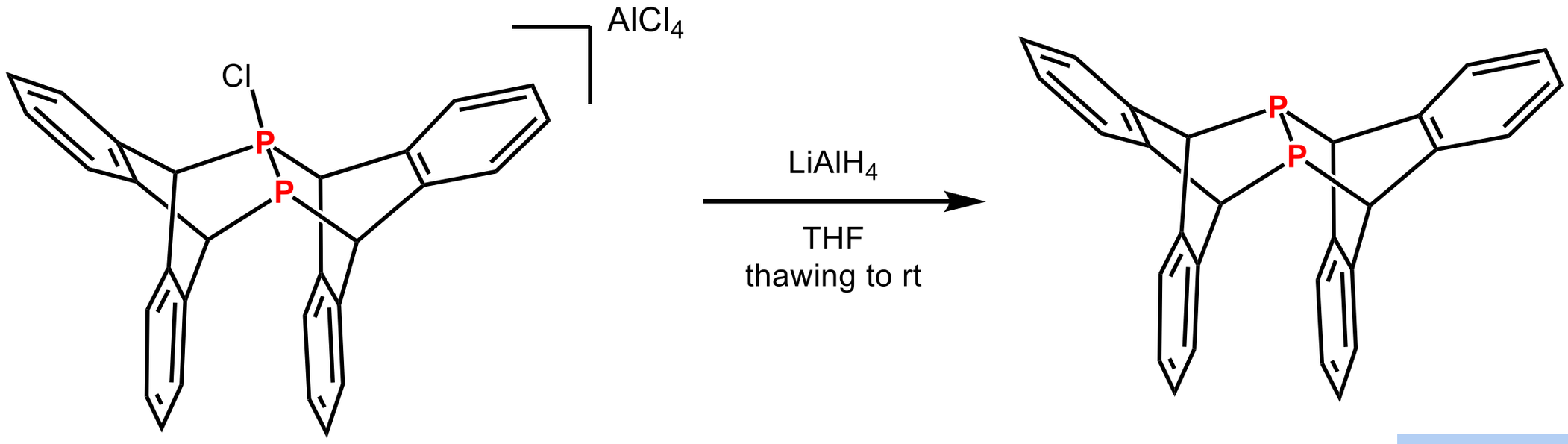
PA chemistry

Synthesis of P_2A_2 and retro Diels−Alder chemistry



89b

94, 28-35%



95, 65%

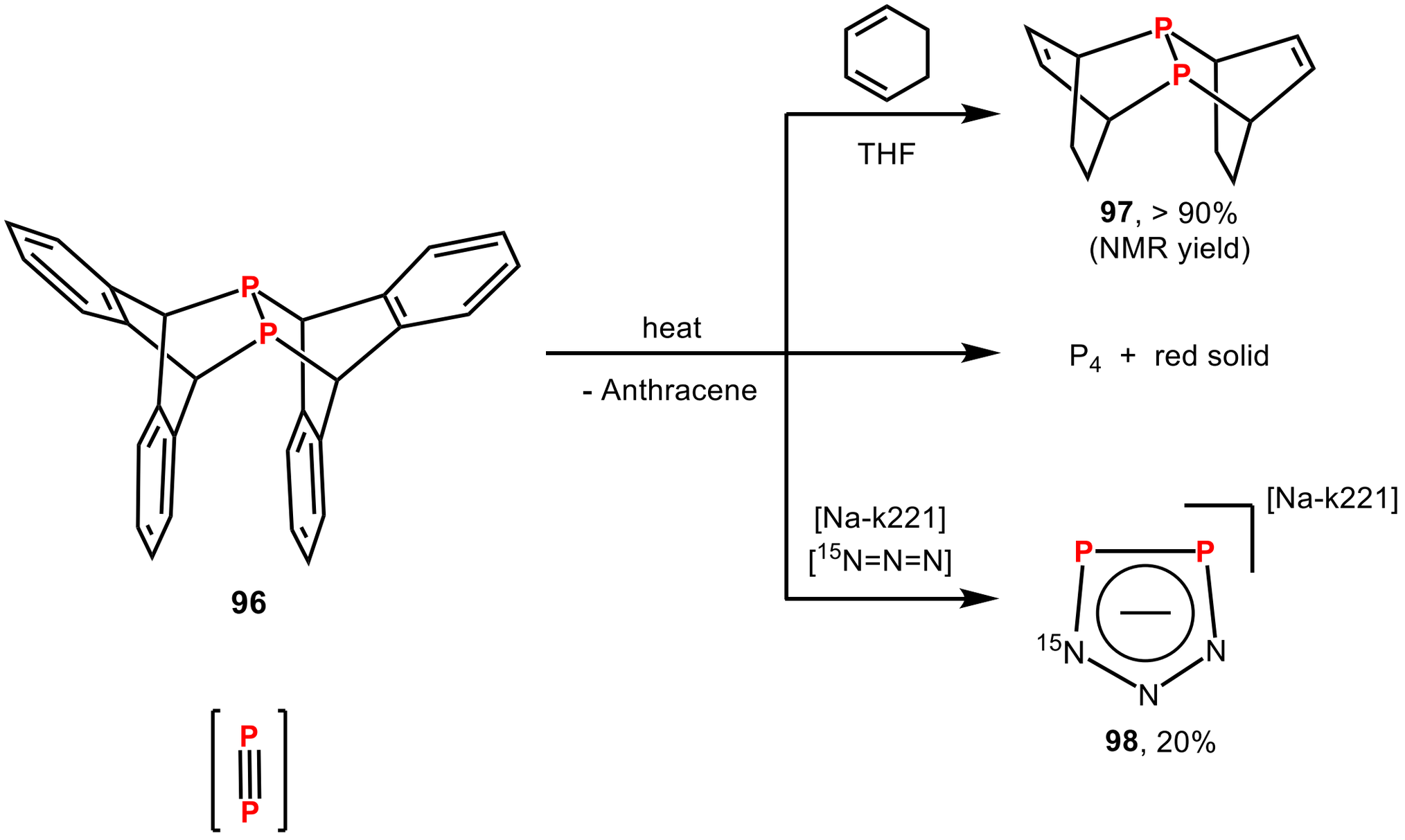
96, 86%

P_2 precursors

Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *136*, 13586.

PA chemistry

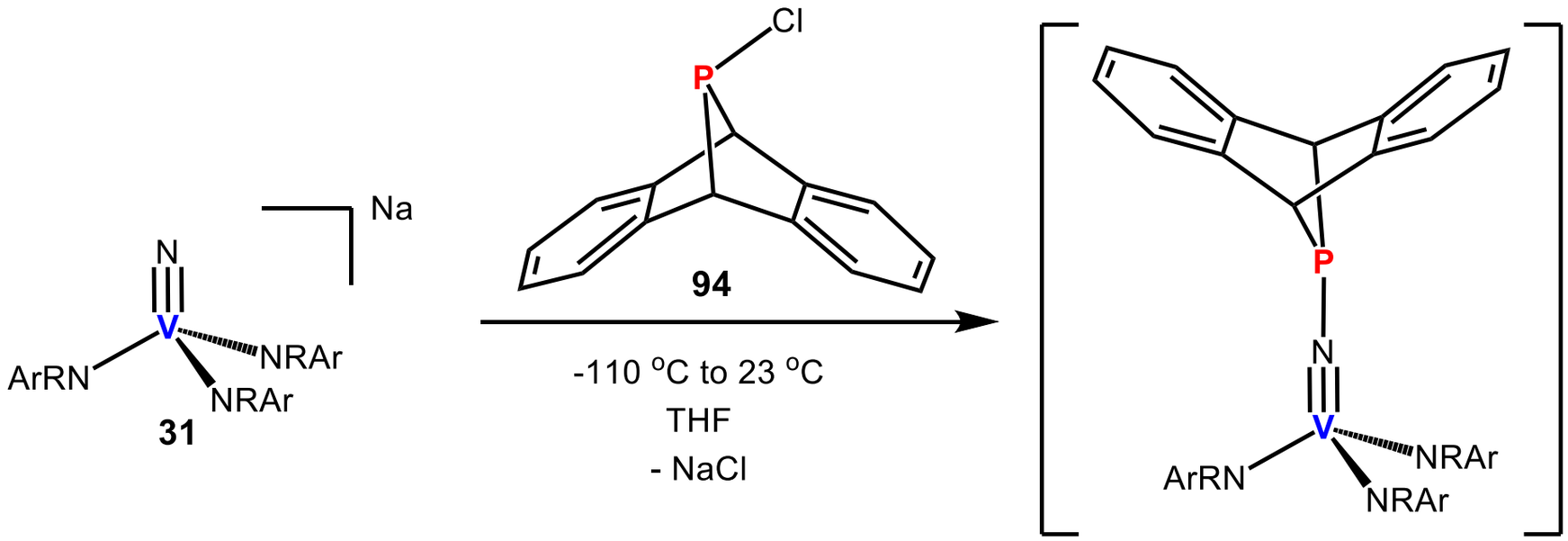
Synthesis of P_2A_2 and retro Diels−Alder chemistry

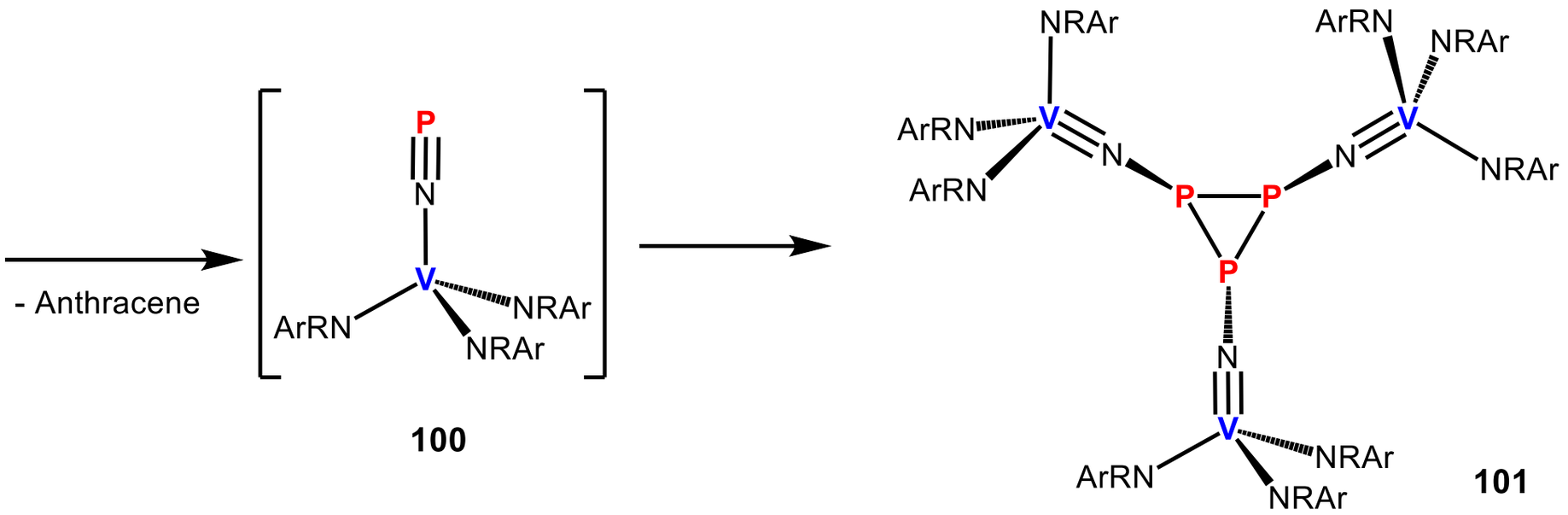


Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *136*, 13586.

PA chemistry

Phosphinidene from ClPA

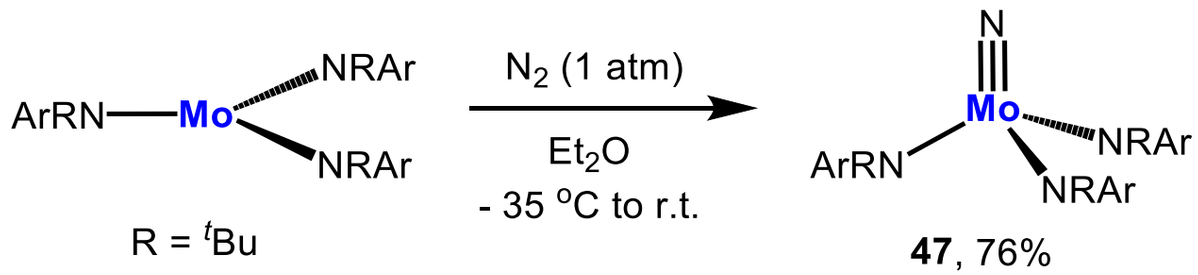


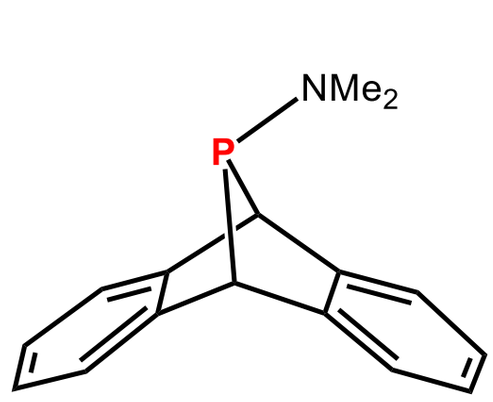


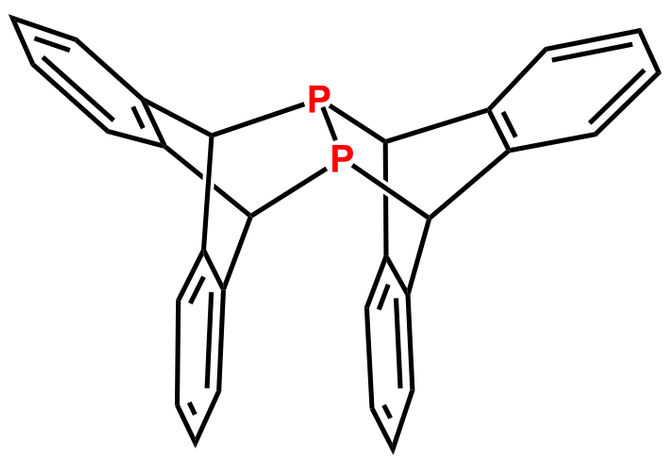
cyclotriphosphane

Courtemanche, M.-A.; Transue, W. J.; Cummins, C. C. *J. Am. Chem. Soc.* **2016**, *138*, 16220.

Summary







Low-coordinated reactive early transition-metal complexes;

Activation of small molecules (N_2, P_4, CO_2, CO, O_2, etc.);

Development of new inorganic functional groups and group transfer reactions;

Detailed studies of key reactions.

Christopher C. Cummins —— Alumni

Ph.D. Graduates

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Prof. Joshua S. Figueroa

Prof. Paula L. Diaconescu

Prof. Jane Brock Greco

Prof. Yi-Chou "James" Tsai

Prof. Daniel J. Mindiola

Prof. Jonas C. Peters

Prof. Aaron L. Odom

Prof. Adam R. Johnson

Prof. Alexandra Velian

Postdoctoral Fellows

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Prof. Luis M. Baraldo

Prof. Mikhail V. Barybin (1999-2001)

Prof. Paul J. Chirik (2000-2001)

Prof. Anthony Cozzolino (2009-2013)

Prof. Nazario Lopez

Prof. Karsten Meyer (1998-2000)

Prof. Michael Montag (2008-2010)

Prof. Tetsuro Murahashi (2003-2005)

Prof. Mostafa Y. Nassar

Thank You!