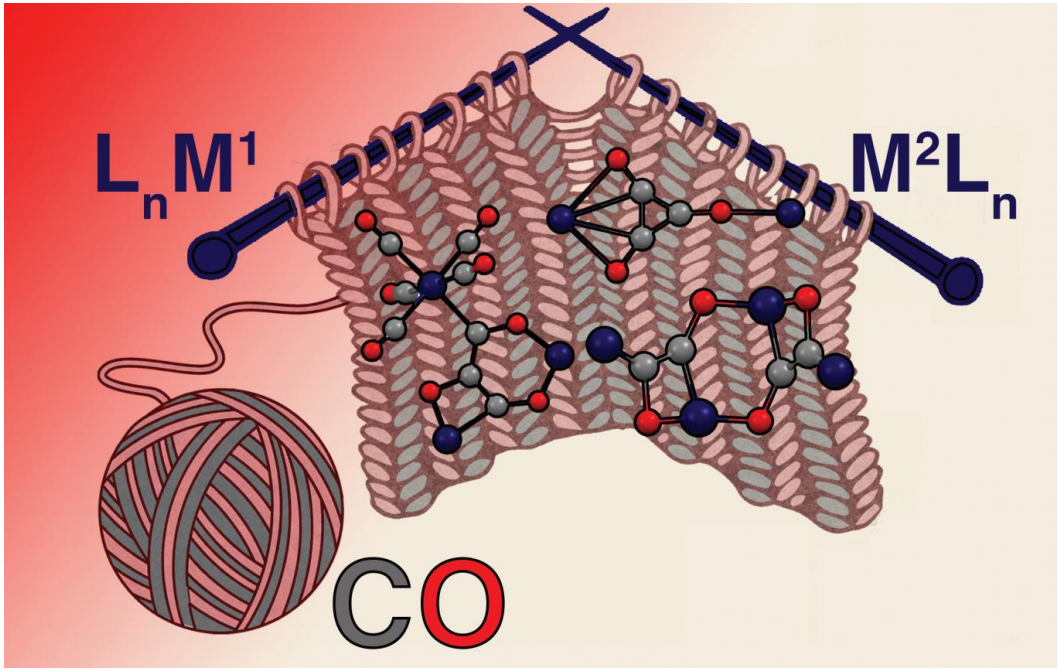
Recent research progress in CO activation with main group elements



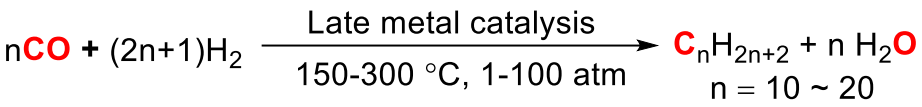
Speaker: Li Ma
Date: 2022-12-02

Contents

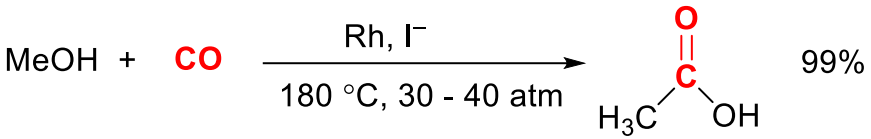
Contents

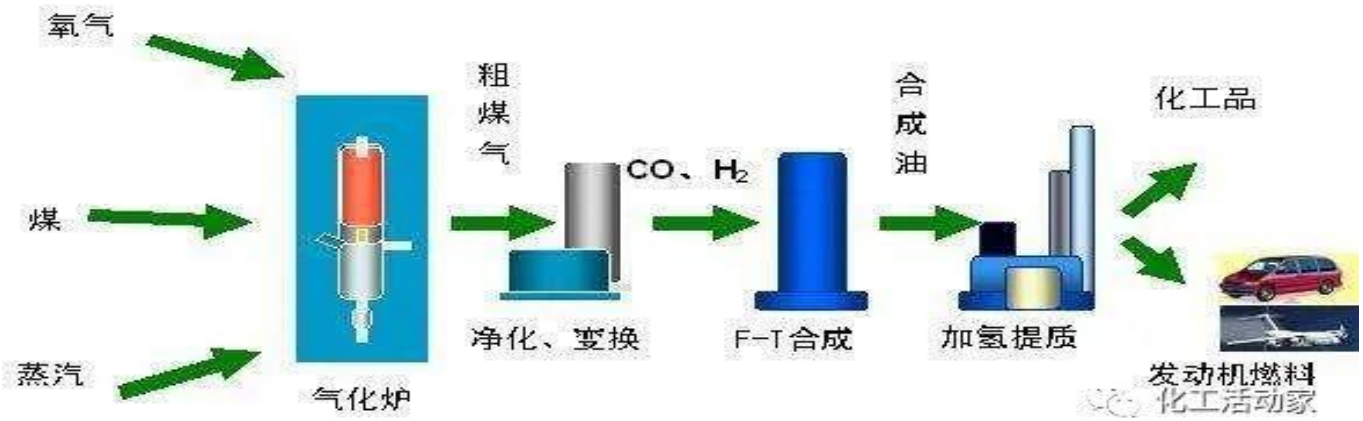
Background

Fischer-Tropsch Process



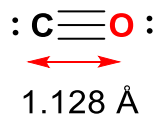
Monsanto Acetic Acid Process



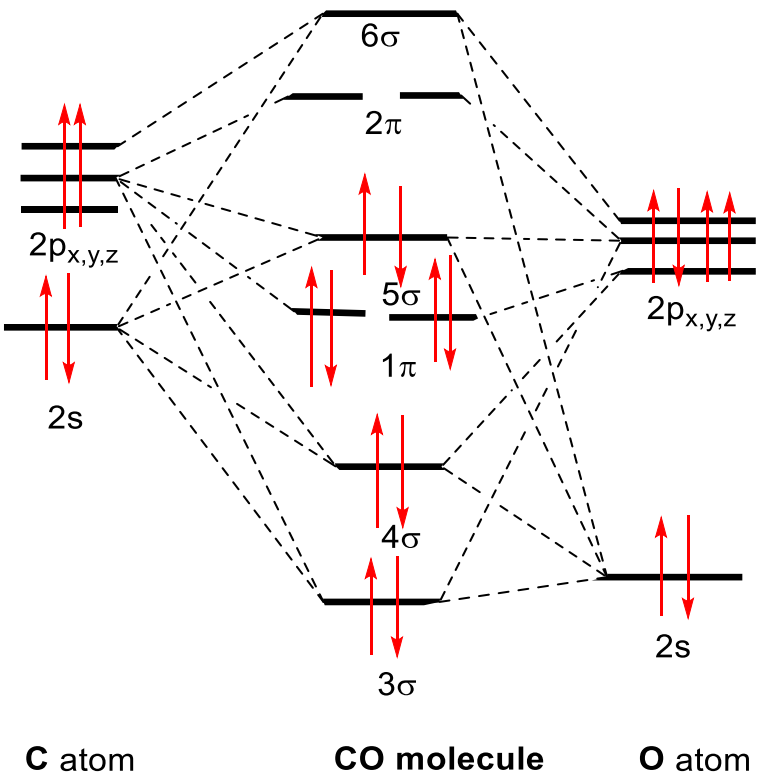


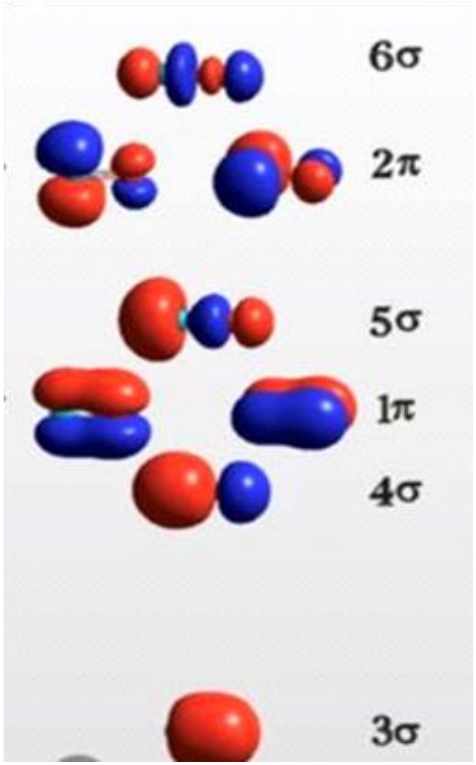
Fongarland, P. et al. *Chem. Rev.* **2007**, *107*, 1692−1744.

Background



BDE = 1072 kcal/mol





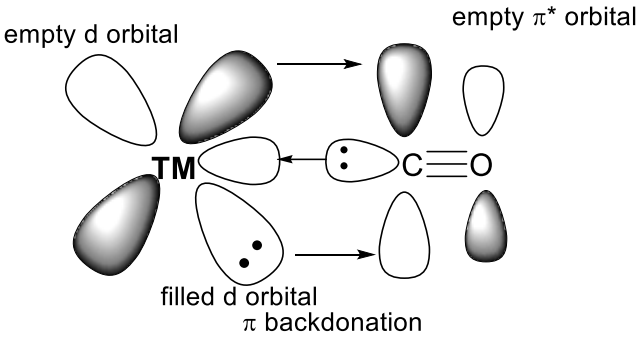
Bond order = (6-0) / 2 = 3

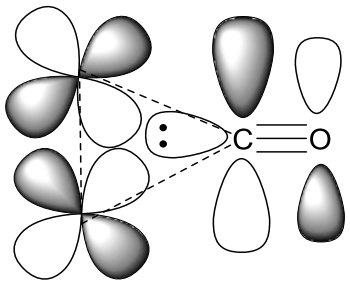
Bond order = (number of bonding electrons - number of antibonding electrons) / 2

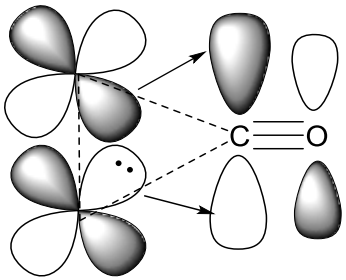
Wu, X.-F. et al. Transition Metal Catalyzed Carbonylation Reactions, *Springer: Germany*, **2013**, 1-234.

Background

Classic bond modes of CO towards transition metals

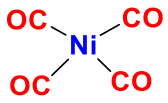


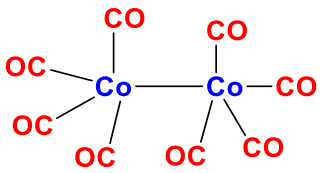




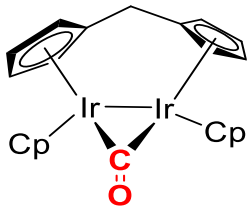
Dewar−Chatt−Duncanson model

Terminal

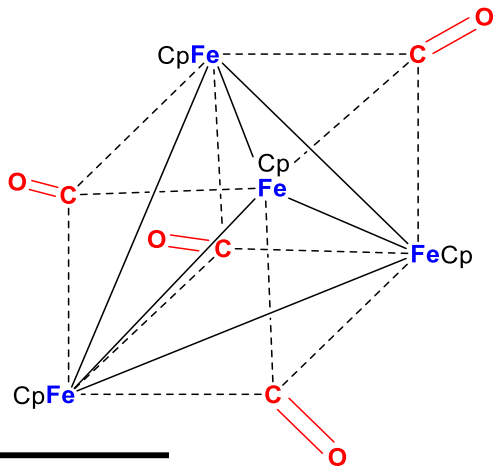




Bridging



μ_2-CO



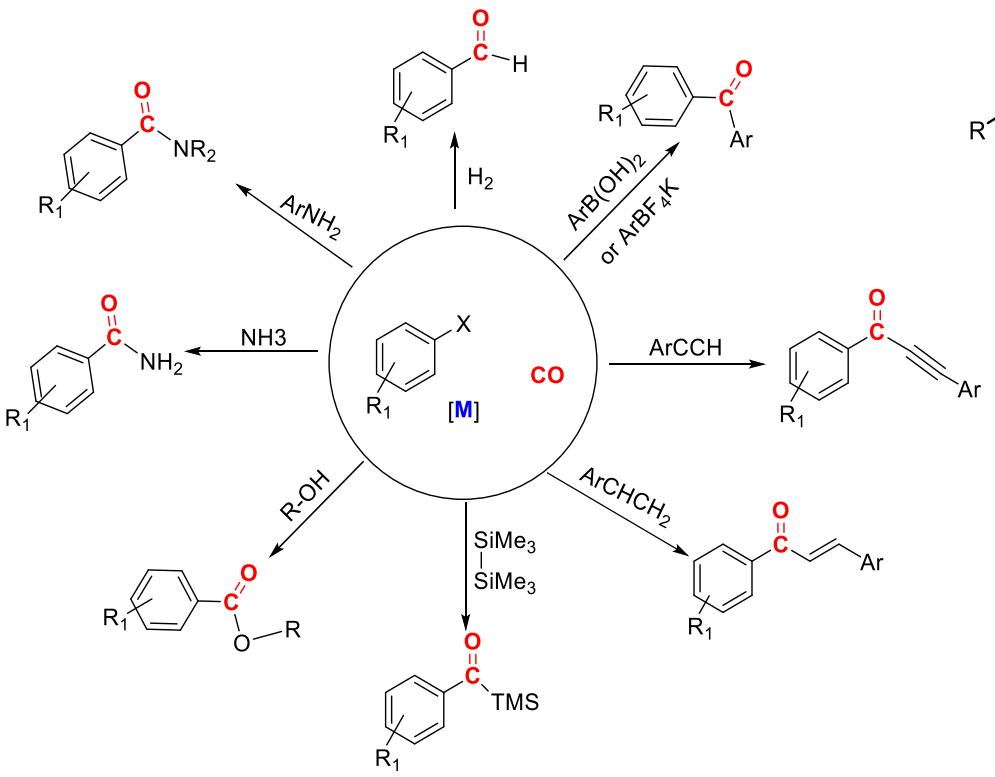
μ_3-CO

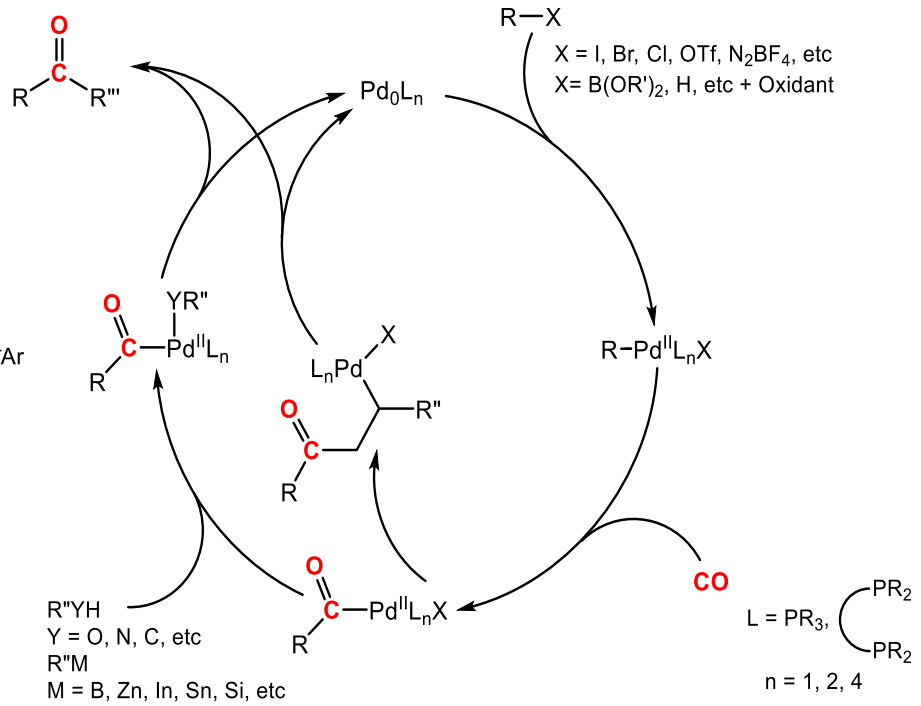
	free CO	Terminal CO	μ2-CO	μ3-CO
d(C-O)	1.128 Å	1.121 Å	1.207 Å	1.197(7)~1.209(7) Å
ν (CO)	2143 cm^{-1}	1850 ~ 2120 cm^{-1}	1700 ~ 1860 cm^{-1}	1620 cm^{-1}

Wu, X.-F. et al. Transition Metal Catalyzed Carbonylation Reactions, *Springer: Germany,* **2013**, 1-234.

Background

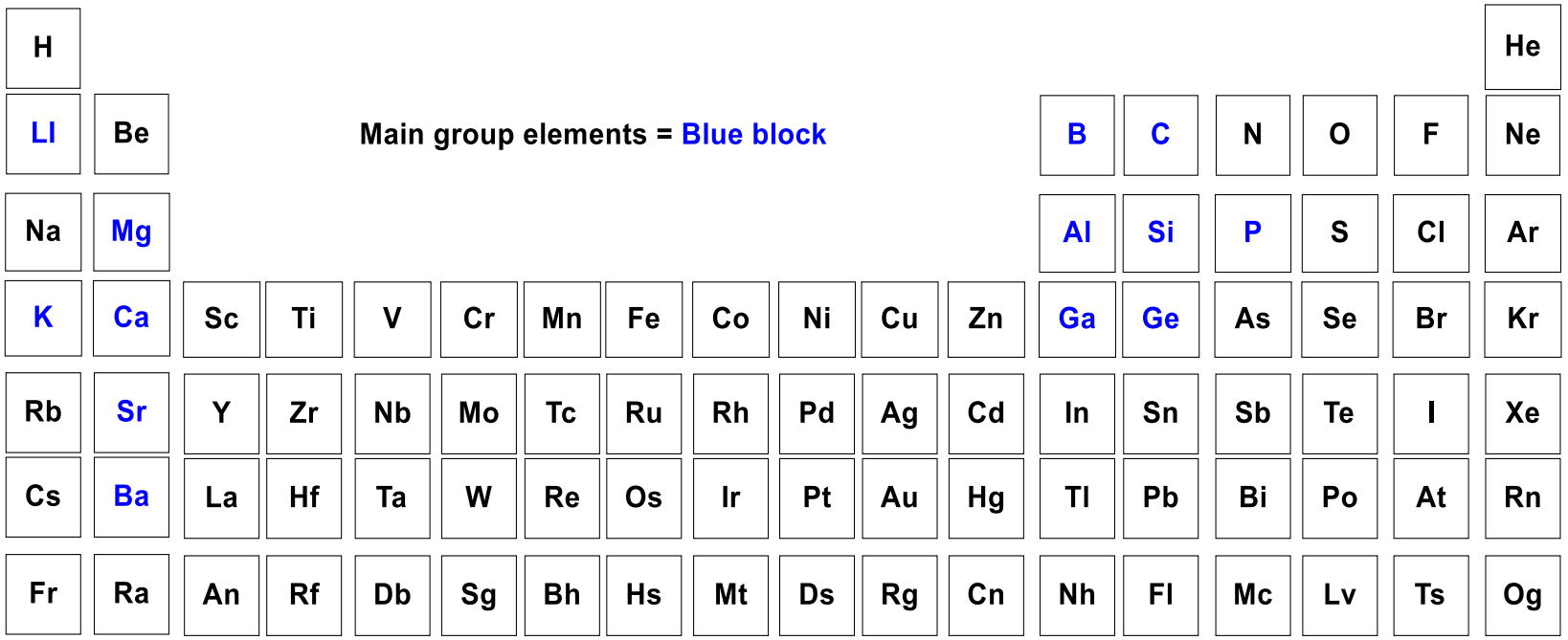
Carbonylation chemistry of late transition metals catalysis





Wu, X.-F. et al. Transition Metal Catalyzed Carbonylation Reactions, Springer: Germany, **2013**, pp1-234.

Background



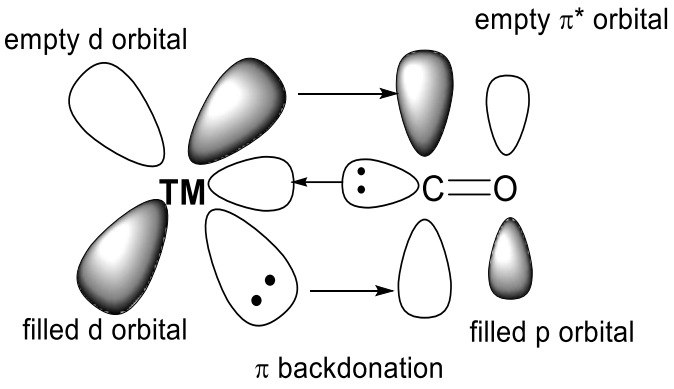
Crustal element abundance

Element	Si (2th)	Al(3th)	Ca(5th)	Na	K	Mg
Crustal content ratio	27.72%	8.13%	3.63%	2.83%	2.59%	2.30%

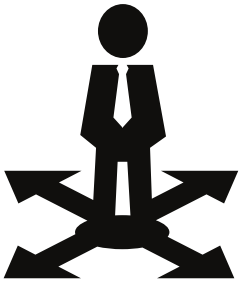
» **Low environmental damage and low cost**
» **High natural abundance**

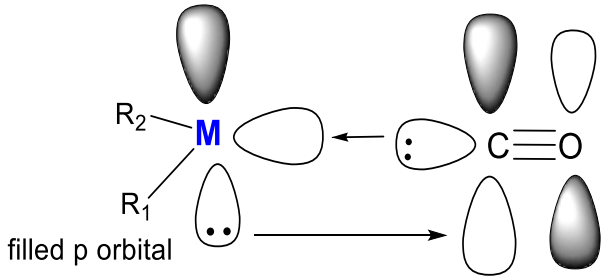
Fongarland, P. et al. *Chem. Rev.* **2007**, *107*, 1692−1744.

Background



Dewar−Chatt−Duncanson model

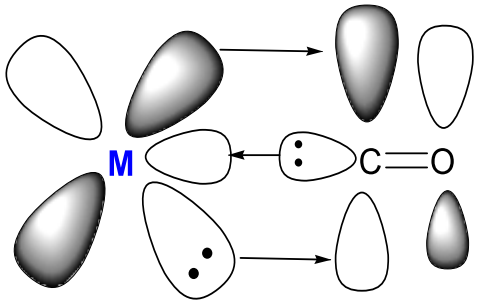




M = main group elements

Low valent species

?

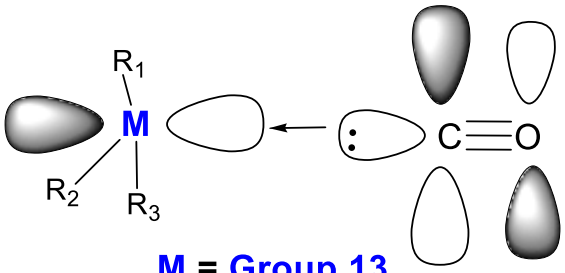


excitation electrons

Ae = alkaline earth

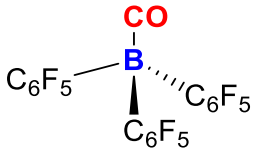
Contents

Introduction



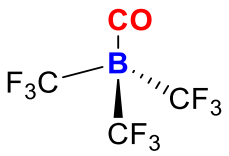
M = Group 13

Lewis acid



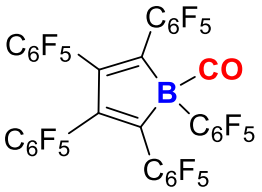
1

ν(CO) = 2241 cm^{-1}



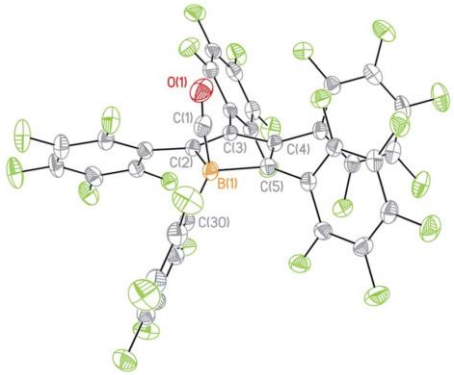
2

ν(CO) = 2252 cm^{-1}



3

ν(CO) = 2231 cm^{-1}



d(free CO) = 1.128 Å

d(C_1–O_1) ≈ 1.115 Å

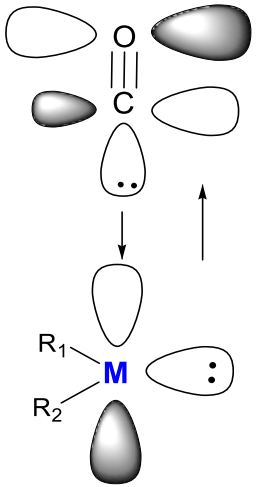
d(B_1–C_1) = 1.609(3) Å

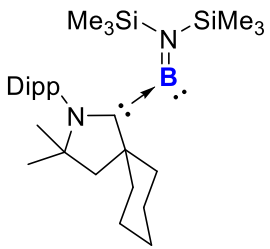
Aubke, F. et al. *J. Am.Chem. Soc.* **2002**, *124*, 15385−15398.

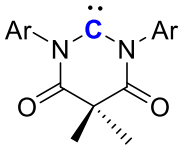
Parvez, M. et al. *Chem. Sci.* **2012**, *3*, 1814−1818.

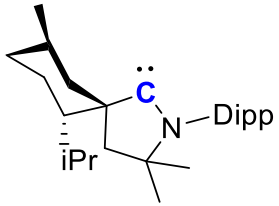
Introduction

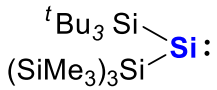
Ambiphilic nature of low-valent species and FLPs

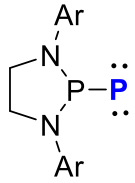






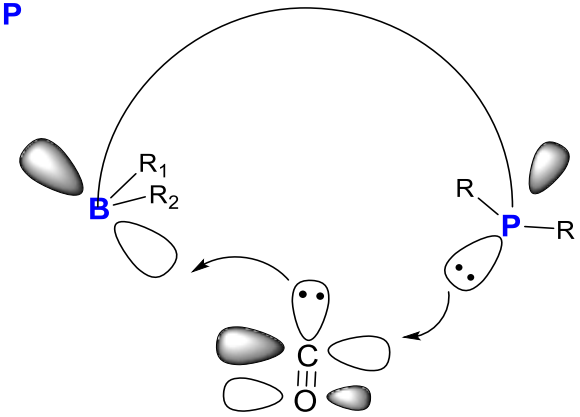


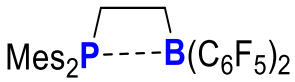




13	14	15
B	C	N
Al	Si	P
Ga	Ge	As

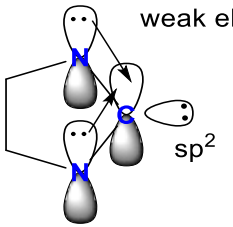
M = B, C, Si, Ge, P



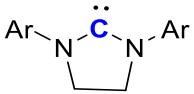


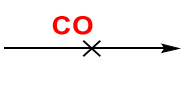
Bertrand, G. et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 3488−3491.
Kutzelnigg, W. et al. *Angew. Chem. Int. Ed.* **1984**, *23*, 272.
Bielawski, C. W. et al. *J. Am. Chem. Soc.* **2009**, *131*, 16039−16041.
Philip, P. P. et al, Nature **2010**, *463,* 171-177.

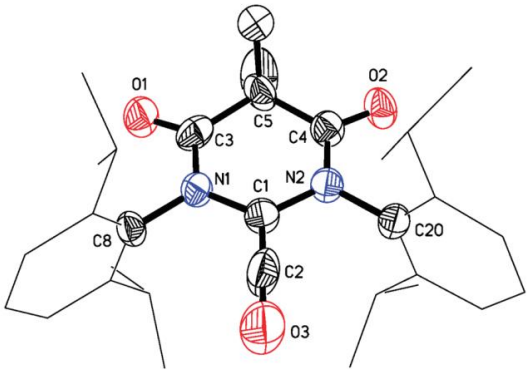
Group 14: Carbene

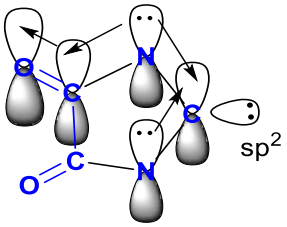


NHCs

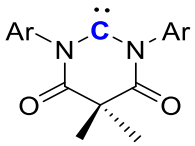


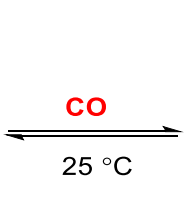


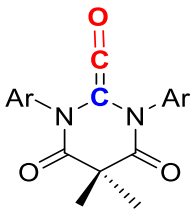




DACs







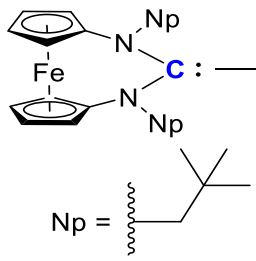
Ar = Dipp or Mes
Mes = 2,4,6-$Me_3C_6H_2$

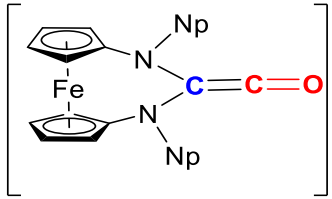
55% conversion
ν = 2100 cm^{-1}

4

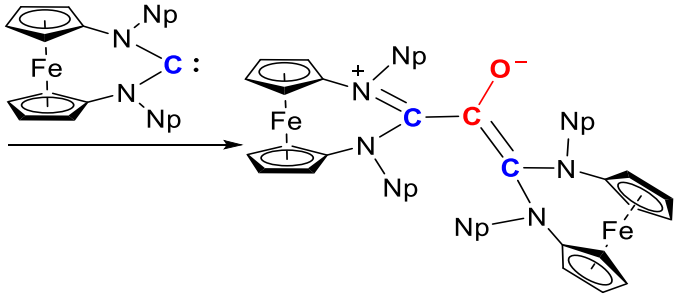
d(free CO) = 1.128 Å
d(C_1-C_2) = 1.302(9) Å
d(C_2-O_3) = 1.182(8) Å

electrophilicity increased





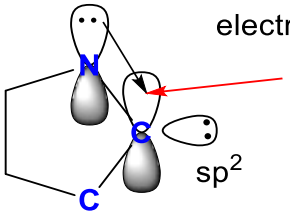
5

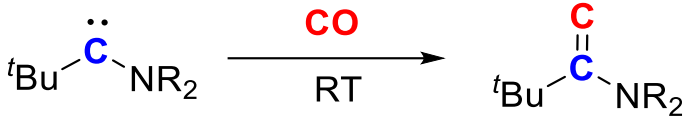


electrophilicity increased

Bertrand, G. et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 3488−3491.
Bielawski, C. W. et al. *J. Am. Chem. Soc.* **2009**, *131*, 16039−16041.
Siemeling, U. et al. *Chem. Sci.* **2010**, *1*, 697−704.

Group 14: Carbene

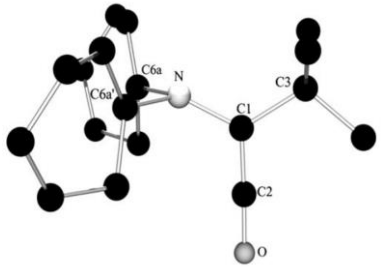




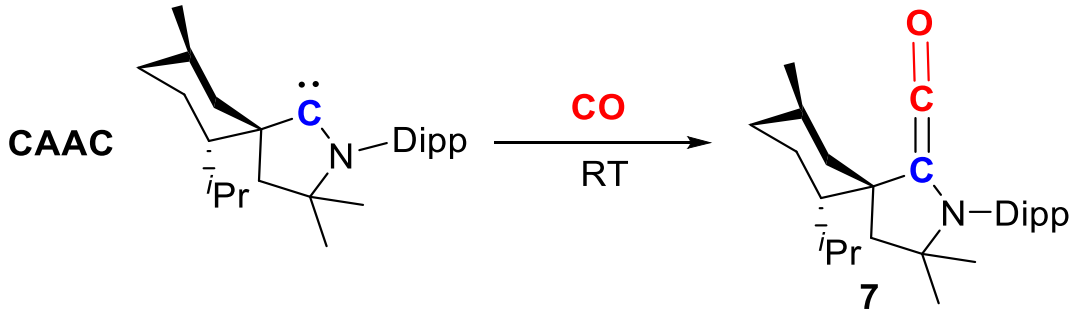
6

R = ^{i}Pr or cyclohexyl

ν = 2066 cm^{-1}



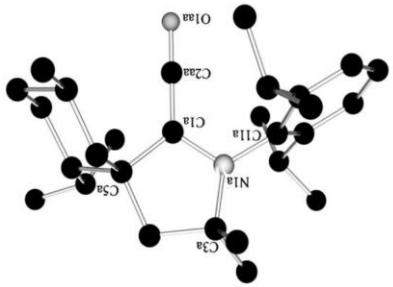
d(free CO) = 1.128 Å
d(C_1–C_2) = 1.310(5) Å
d(C_2–O) = 1.174(4) Å



7

Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$

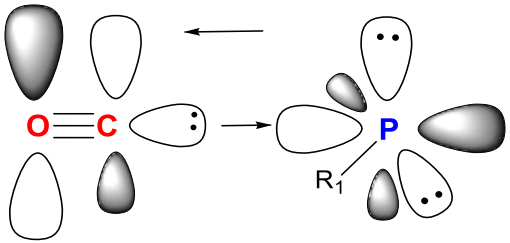
ν = 2073 cm^{-1}

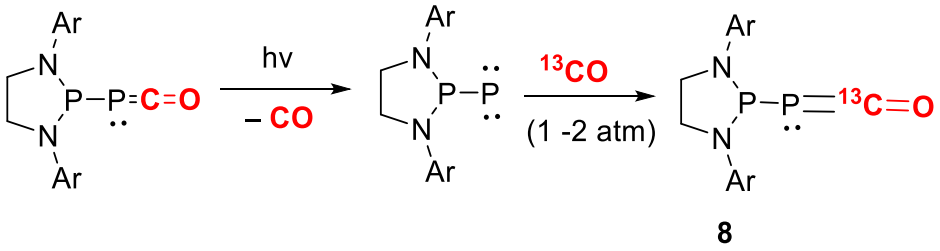


d(free CO) = 1.128 Å
d(C_1–C_2) = 1.334(5) Å
d(C_2–O_1) = 1.186(5) Å

Bertrand, G. et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 3488−3491.
Bielawski, C. W. et al. *J. Am. Chem. Soc.* **2009**, *131*, 16039−16041.

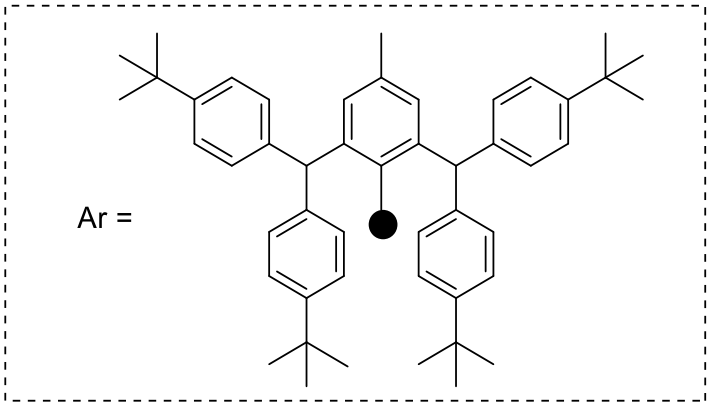
Singlet (Phosphino)phosphinidenes are Electrophilic

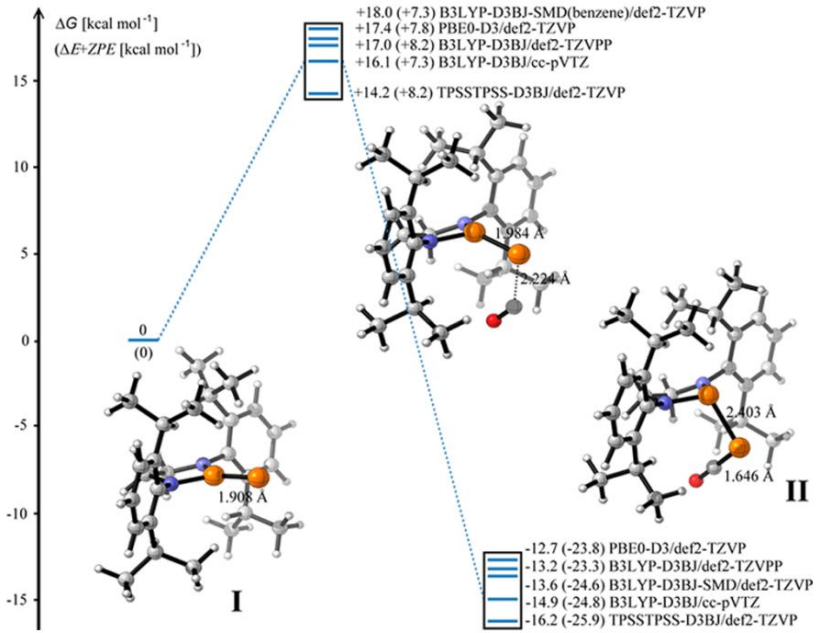




8

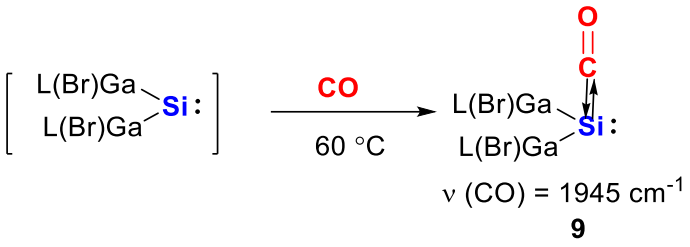
ν = 1875 cm^{-1}

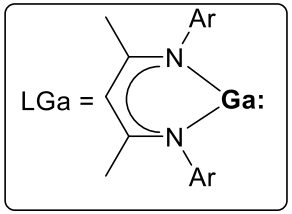


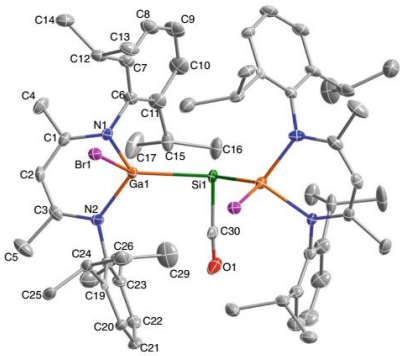


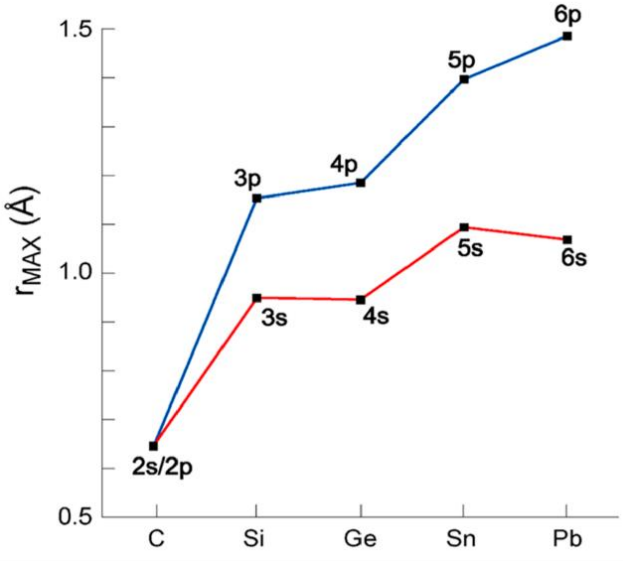
Bertrand, G. et al. *J. Am. Chem. Soc.* **2016**, *138*, 8356−8359.

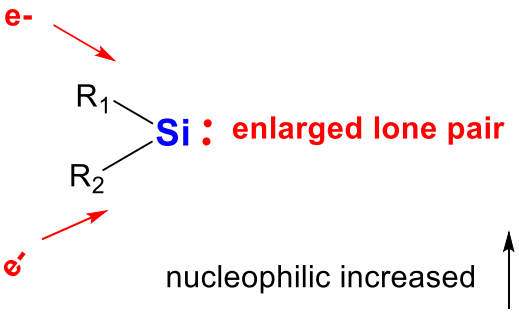
Group 14: Silylene







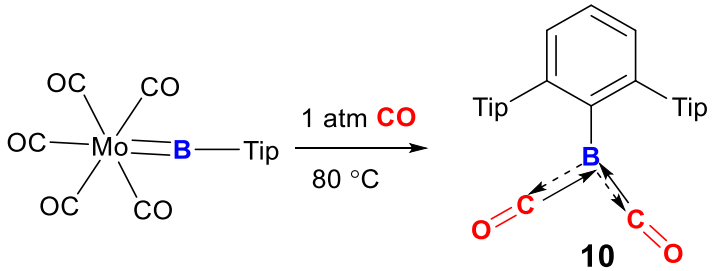




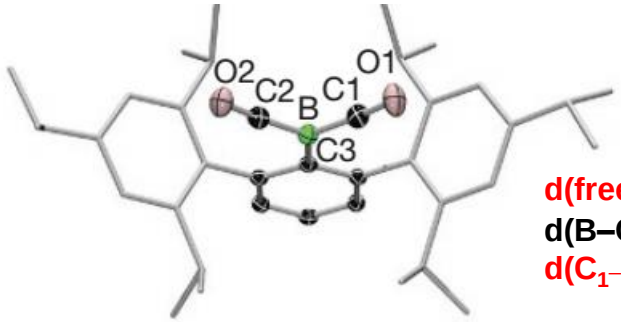
d(free CO) = 1.128 Å
d(C-O) = 1.136(7) Å

Schreiner, R. P. et al. *Nat. Chem.* **2020**, *12*, 608−614.
Inoue, S. et al. *Nat. Chem.* **2020**, *12*, 1131−1135.
Aldridge, S. et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 1808−1812.

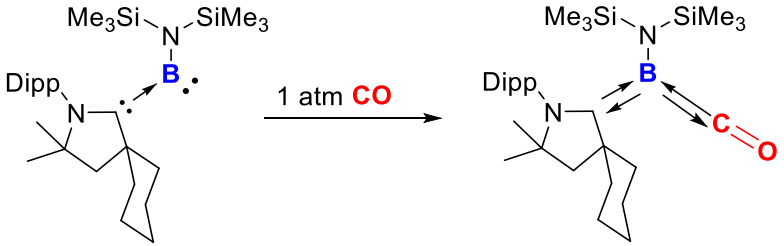
Group 13: Borylene



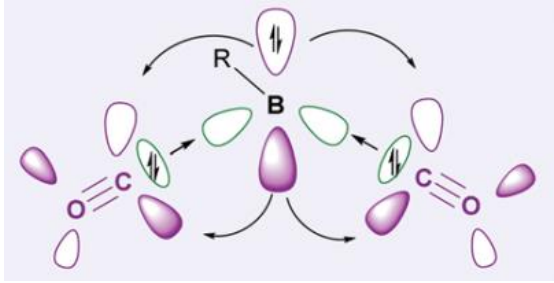
10

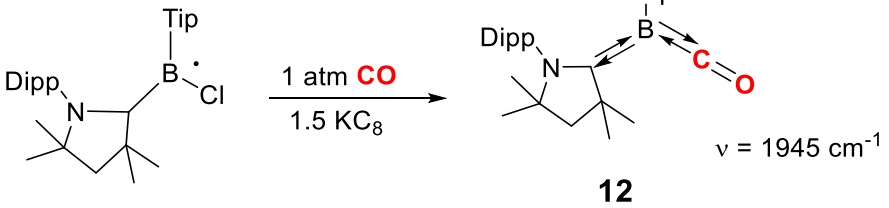


d(free CO) = 1.128 Å
d(B–C) = 1.473(3)~1.475(3) Å
d(C_1–O_1) = 1.150(2)~1.152(2) Å

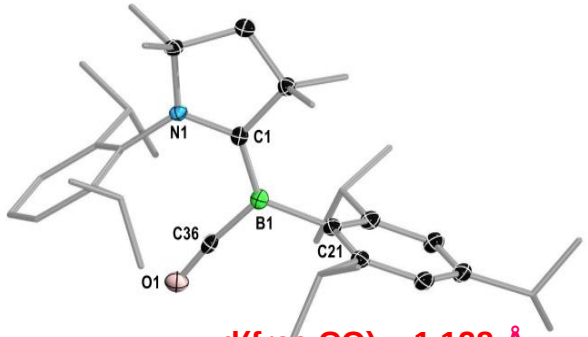


11 ν = 1956 cm^{-1}





12 ν = 1945 cm^{-1}



d(free CO) = 1.128 Å
d(C_{36}–O_1) = 1.1461(15) Å
d(B_1-C_{36}) = 1.4857(18) Å
d(C_1–B_1) = 1.5047(17) Å

Braunschweig, H. et al. *Nature* **2015**, *522*, 327−330.
Stephan, D. W. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159−13163.
Braunschweig, H. et al. *Angew. Chem., Int. Ed.* **2021**, *60*, 2963−2968.

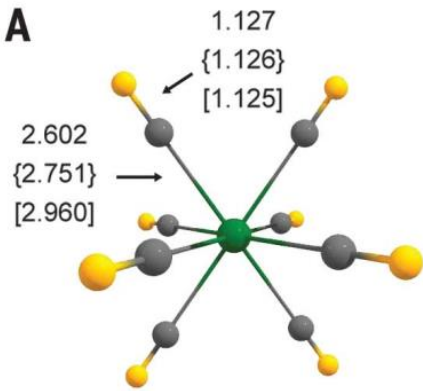
M$(CO)_8$

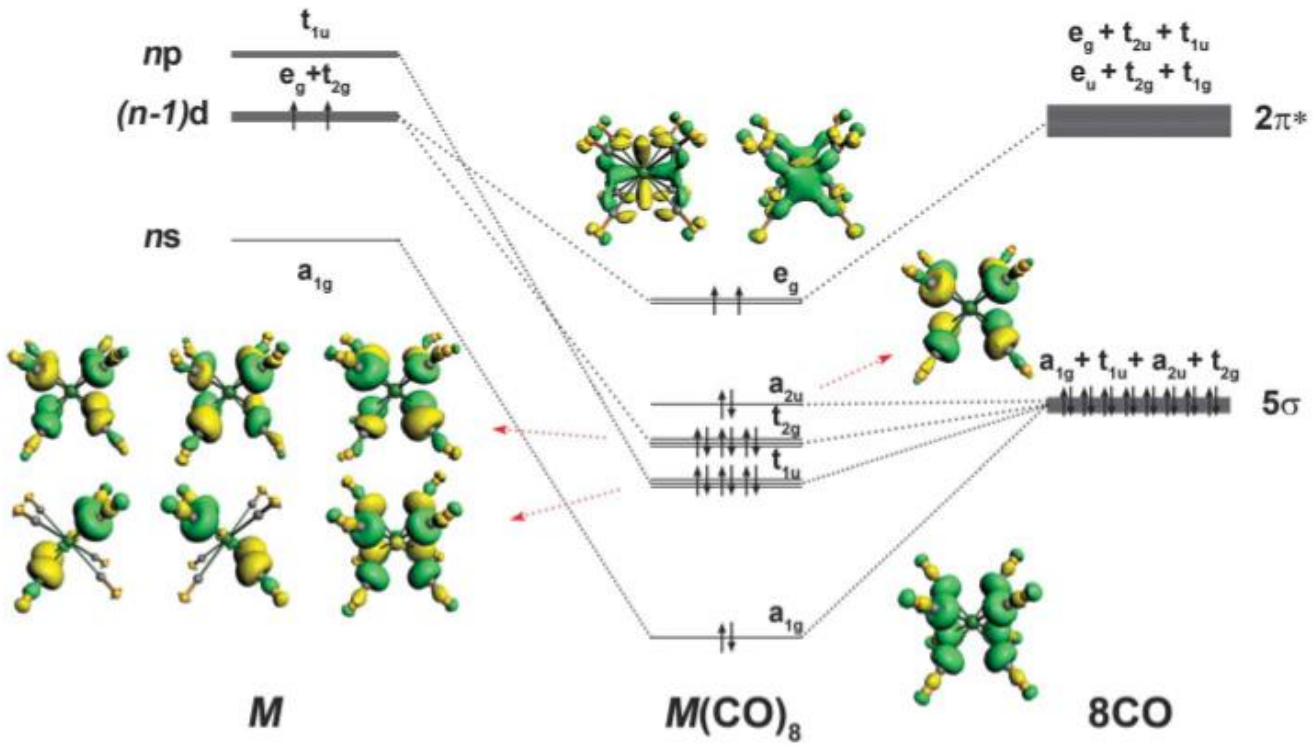
M = Ca, Sr, Ba

ν $(Ca(CO)_8)$ = 1987 cm^{-1}

ν $(Sr(CO)_8)$ = 1995 cm^{-1}

ν $(Ba(CO)_8)$ = 2014 cm^{-1}

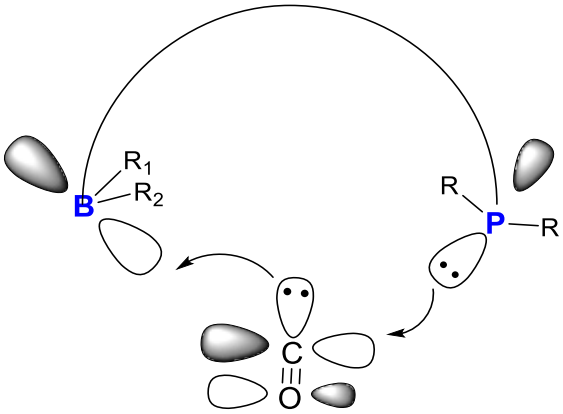


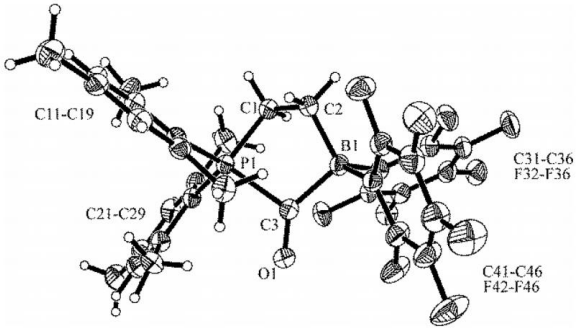


	Ca	Sr	Ba
$\Delta E_{prep(b)}$ $M,ns^2 \rightarrow ns^0(n-1)d^2(T)$	159.5	150.9	68.2

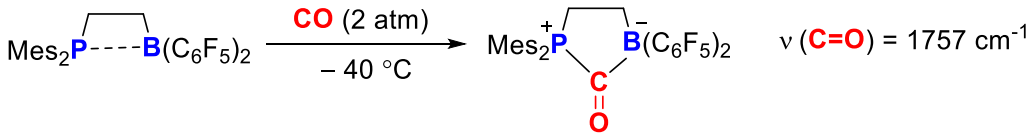
Calculated method: M06-2X/TZ2P-ZORA

Zhou, M. et al. *Science* **2018**, *361*, 912–916.

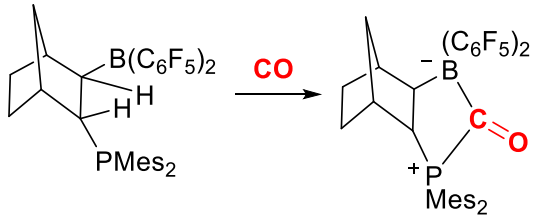




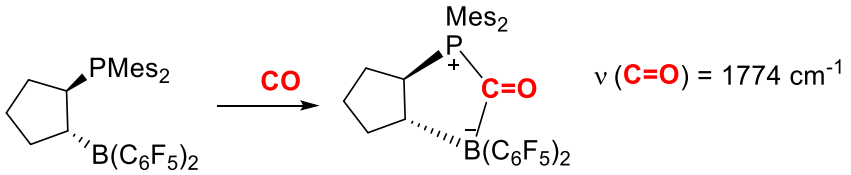
d(free CO) = 1.128 Å
d(C_3-O_1) = 1.191(2) Å



13



14 ν (**C=O**) = 1791 cm^{-1}

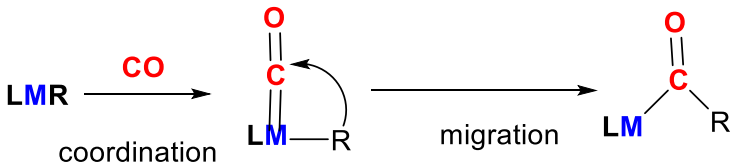


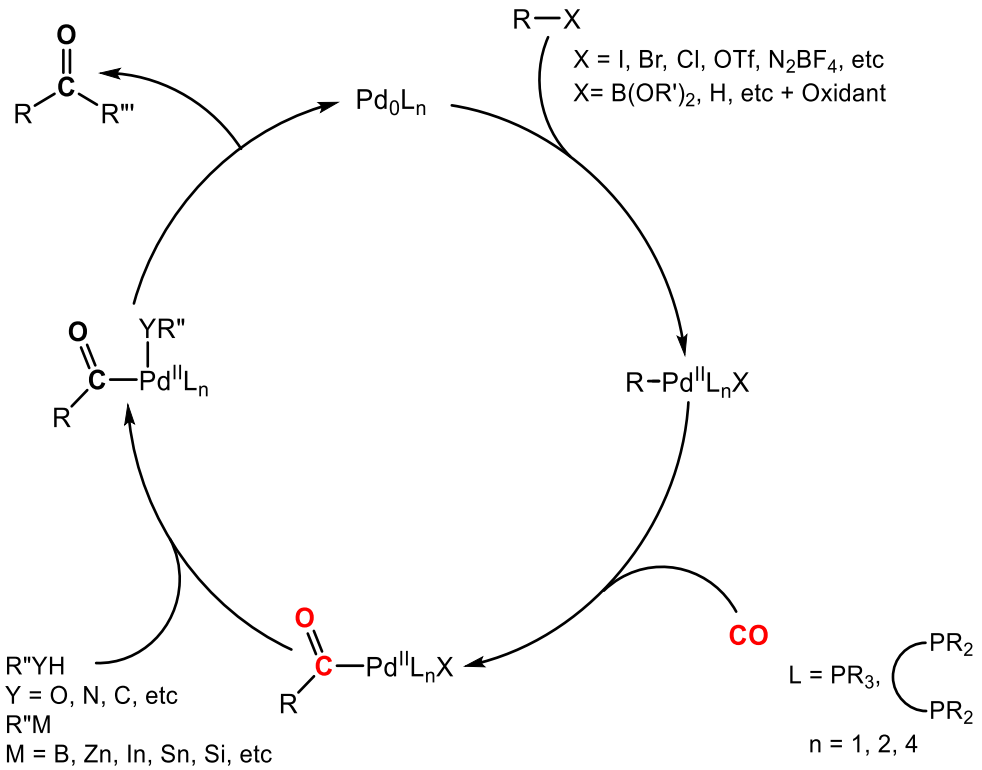
15

Erker, G. et al. *J. Am. Chem. Soc.* **2013**, *135*, 18567−18574.
Erker, G. et al. *J. Am. Chem. Soc.* **2020**, *142*, 17260−17264.

Contents

Introduction

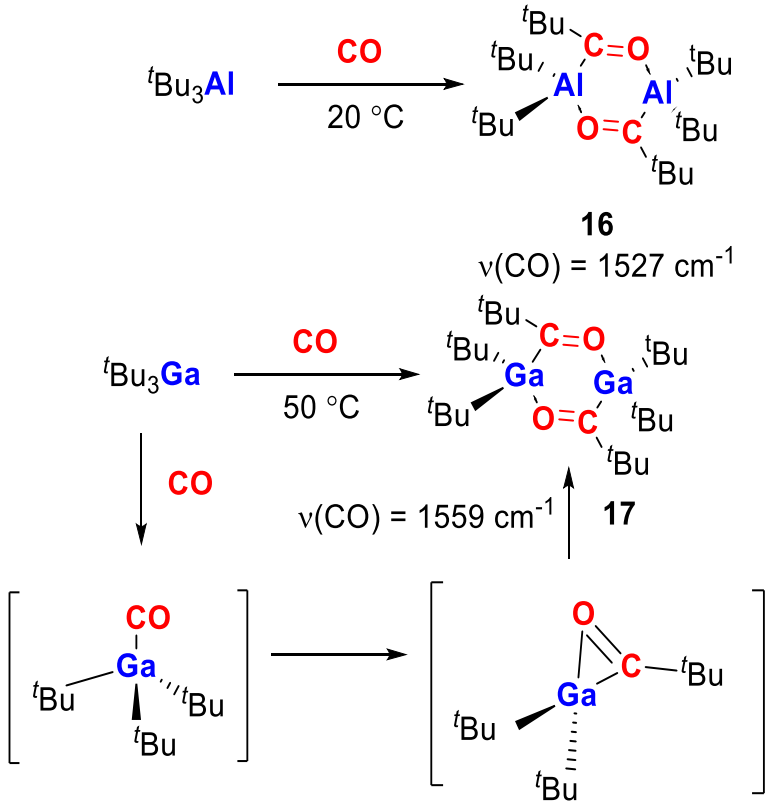


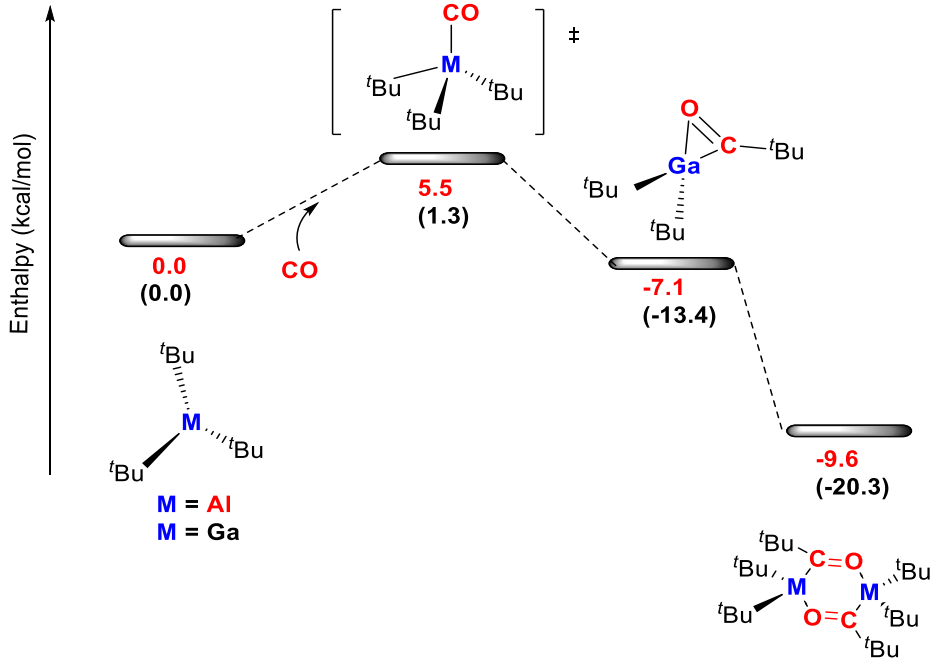


Wu, X.-F. et al. Transition Metal Catalyzed Carbonylation Reactions, *Springer: Germany*, **2013**, 1-234.

Insertion reaction

Alkyl aluminium / Alkyl gallium



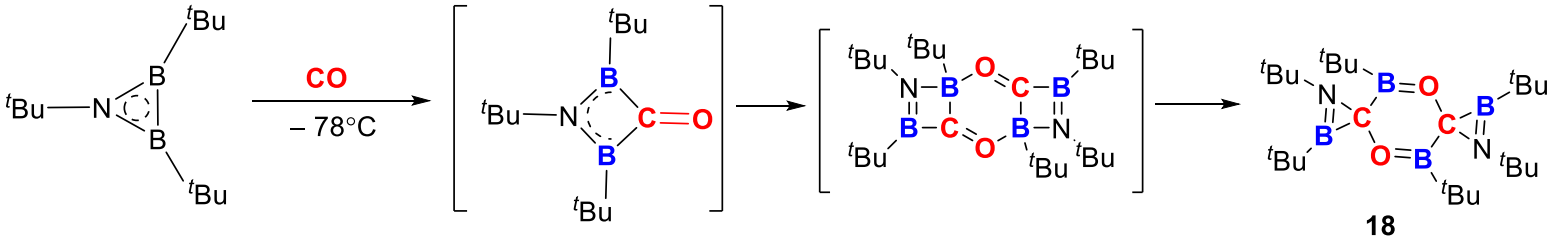


d(free CO) = 1.128 Å
d(Al-C) = 2.007(4) Å
d(C=O) = 1.252(3) Å

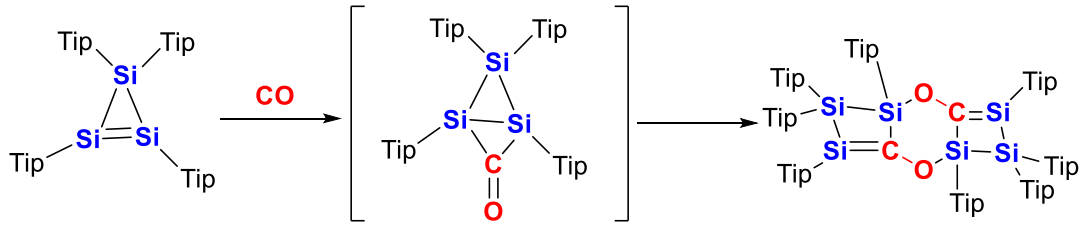
d(Ga-C) = 2.017(7) Å
d(C=O) = 1.249(3) Å

Kirschbaum, K. et al. *J. Am. Chem. Soc.* **2004**, *126*, 11812−11813.
Hu, X. et al. *Inorg. Chim. Acta.* **2008**, *361, 3332*− 3337.

Insertion reaction

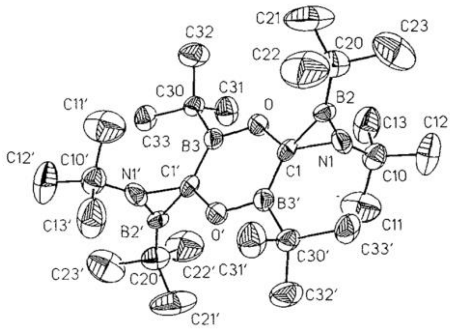


18



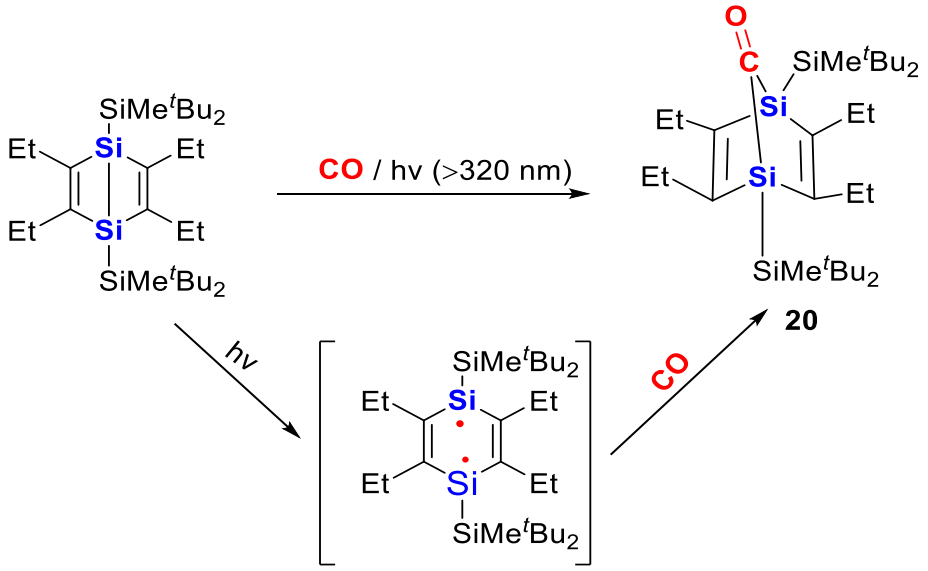
Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$

19



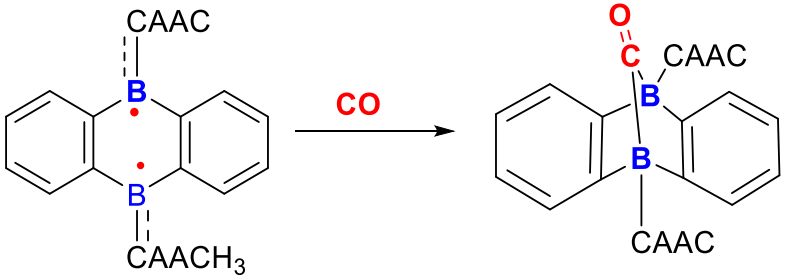
d(free CO) = 1.128 Å
d(B-O) = 1.360(5) Å
d(O-C) = 1.453(5) Å

Boese, R. et al. *Angew. Chem. Int. Ed.* **1990**, *29*, 900−902.
Sekiguchi, A. et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 13247−13250.

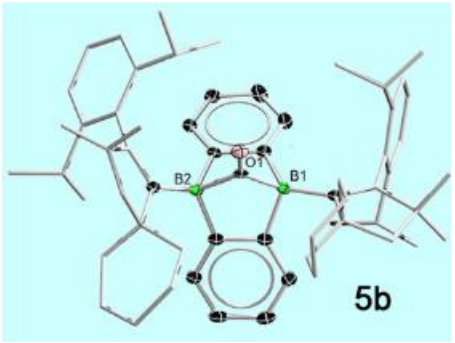


ν = 1673 cm^{-1}

d(free CO) = 1.128 Å
d(C=O) = 1.199(2) Å
d(Si-C) = 1.9730(17) Å



ν (CO) = 1690 cm^{-1}

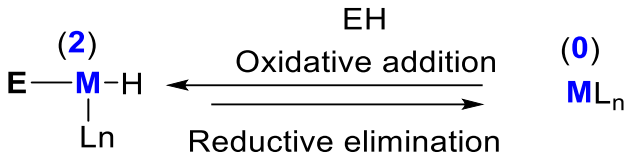


d(free CO) = 1.128 Å
d(B-C_{CO}) = 1.695(3) Å
d(C=O) = 1.205(2) Å

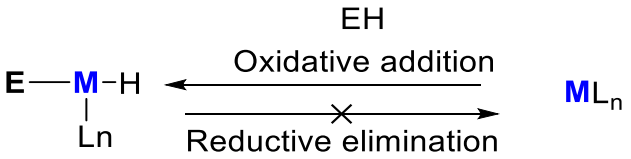
Sekiguchi, A. et al. *Organometallics* **2005**, *24*, 3368−3370.
Braunschweig, H. et al. *Angew.Chem. Int. Ed.* **2020**, *59*,19338–19343.

Contents

transition metals **vs** **main group elements**



M = low valent transition metal

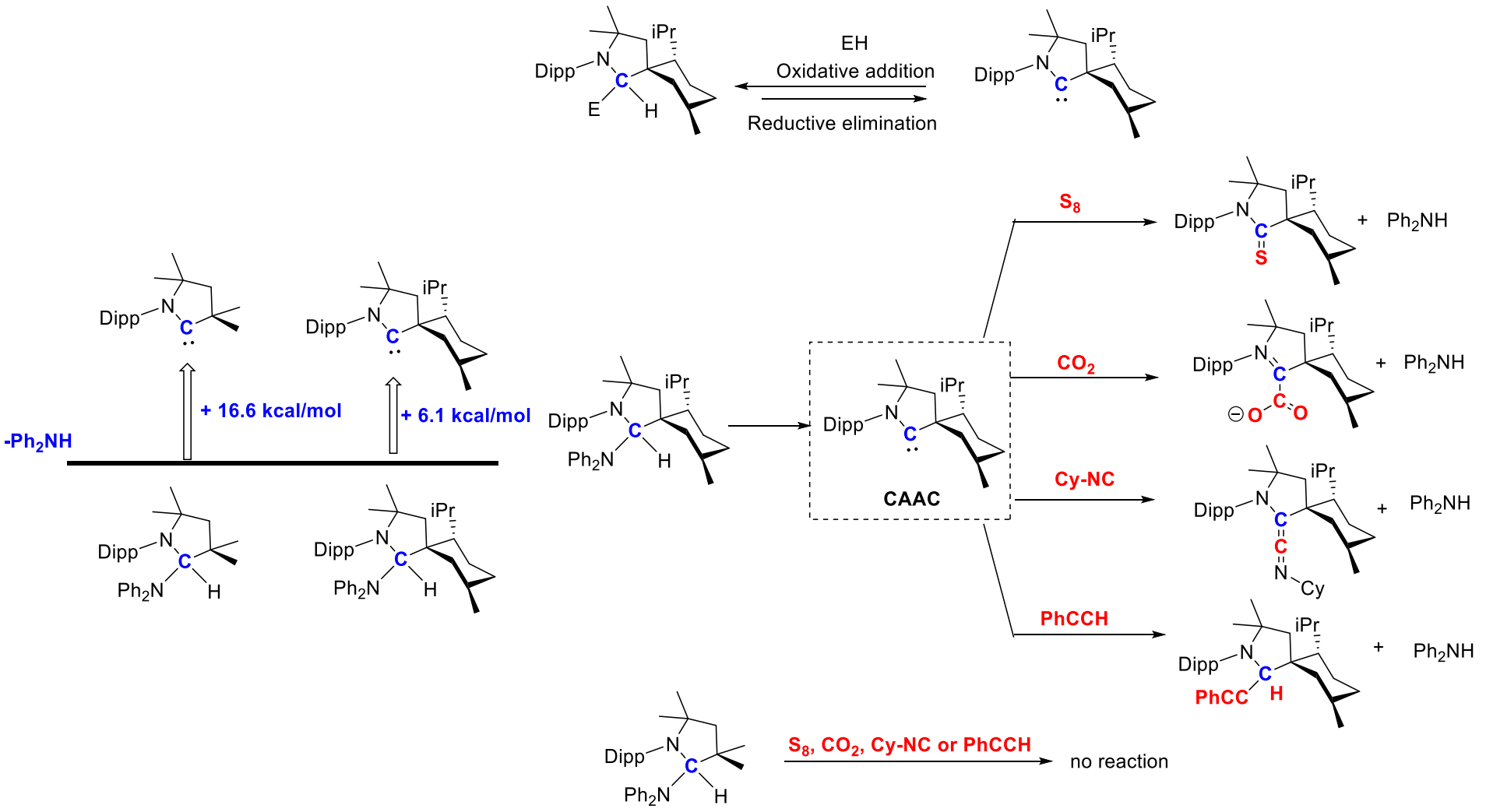


M = low valent main group metals

Nikonov, G. I. et al. *Chem. Rev.* **2018**, *118*, 3608−3680.

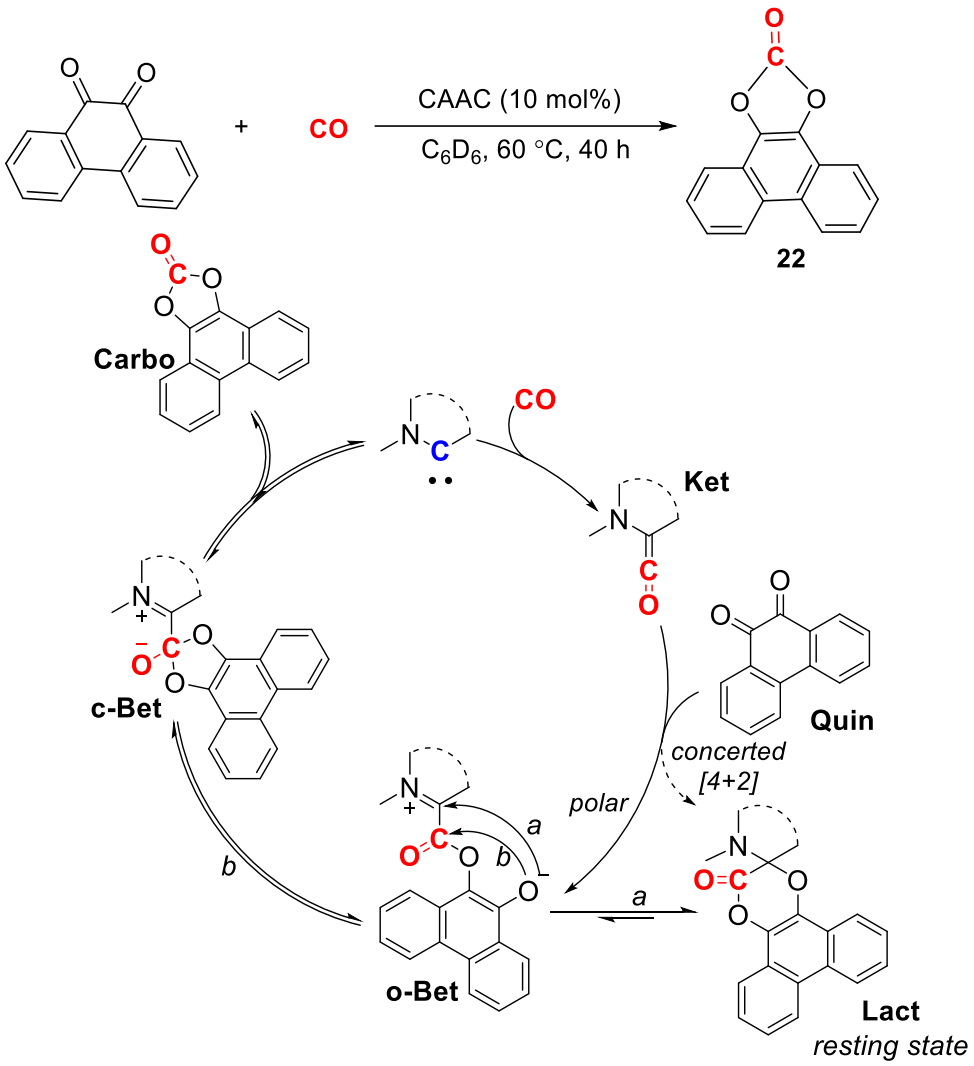
Introduction

Reductive elimination at a carbon center under steric control



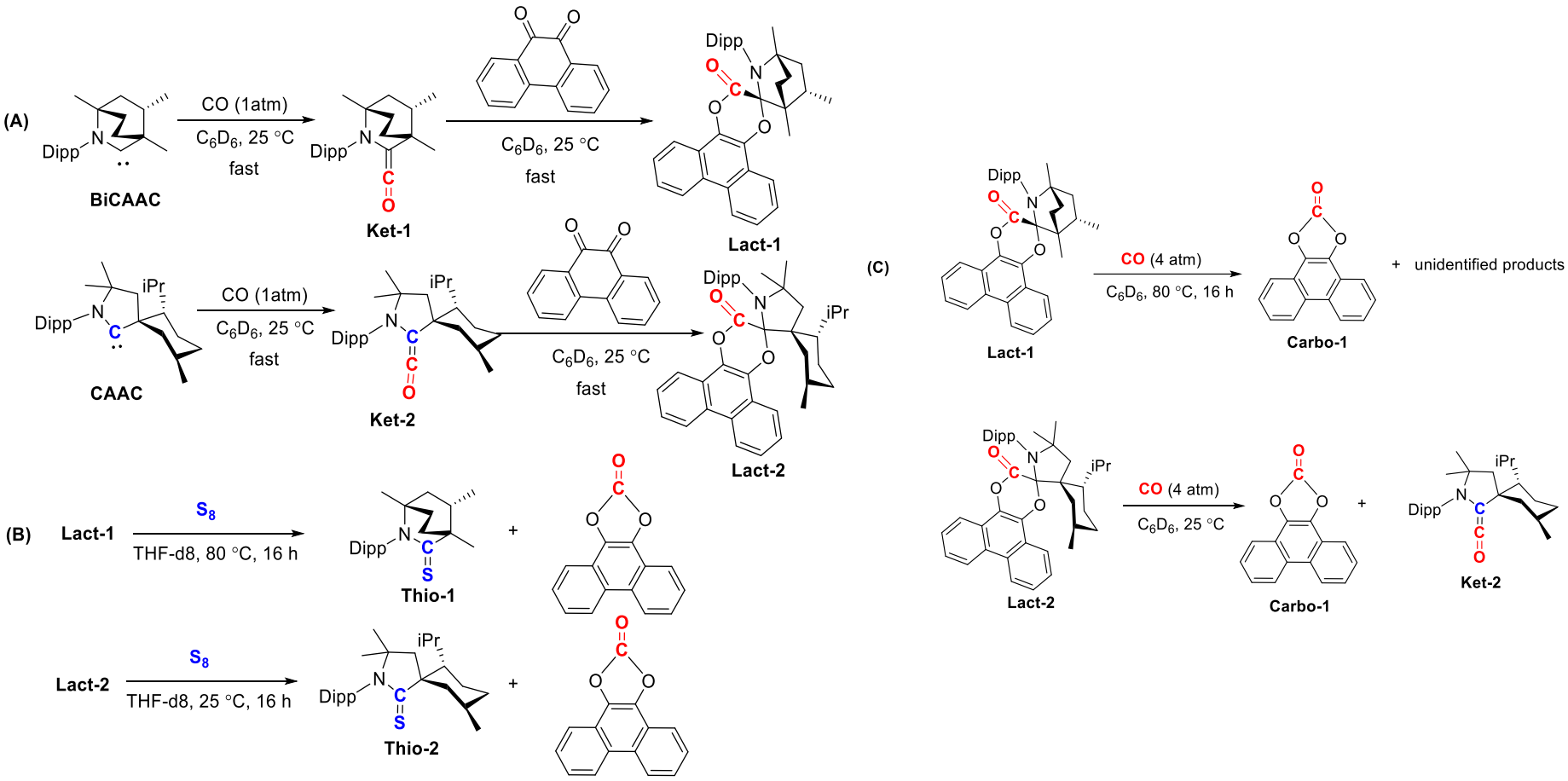
Bertrand, G. et al. *J. Am. Chem. Soc.* **2019**, *141*, 9823−9826.

Metal free Carbene-catalyzed carbonylation with Gaseous CO



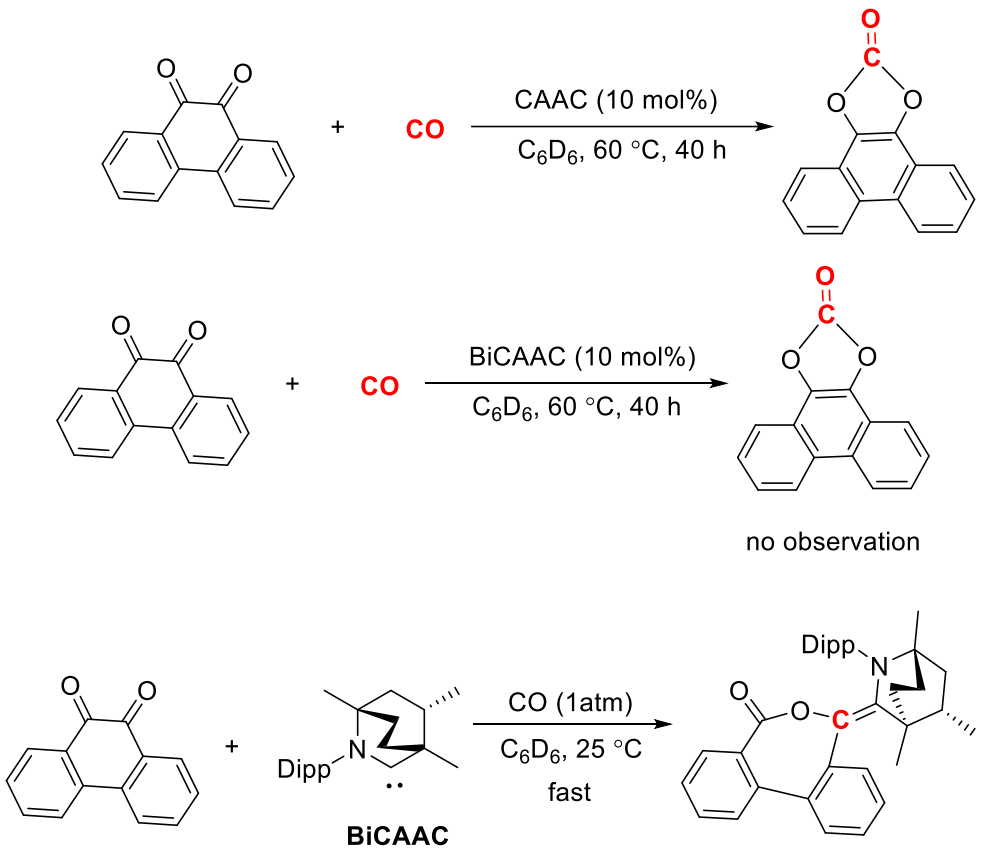
Bertrand, G. et al. *J. Am. Chem. Soc.* **2020**, *142*, 18336−18340.

Validation of elementary steps



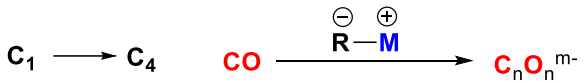
Bertrand, G. et al. *J. Am. Chem. Soc.* **2020**, *142*, 18336−18340.

Metal free Carbene-catalyzed carbonylation with Gaseous CO

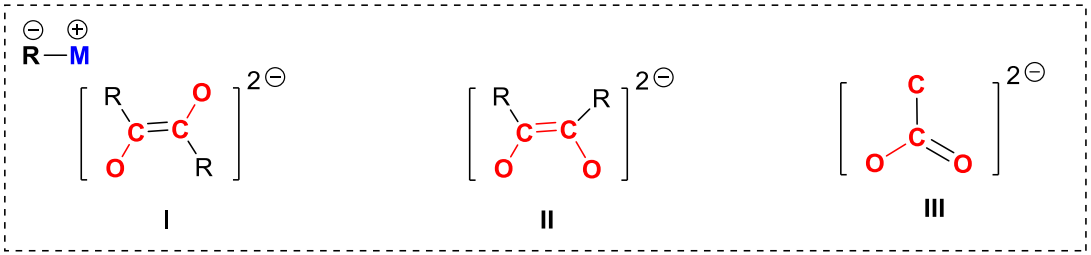


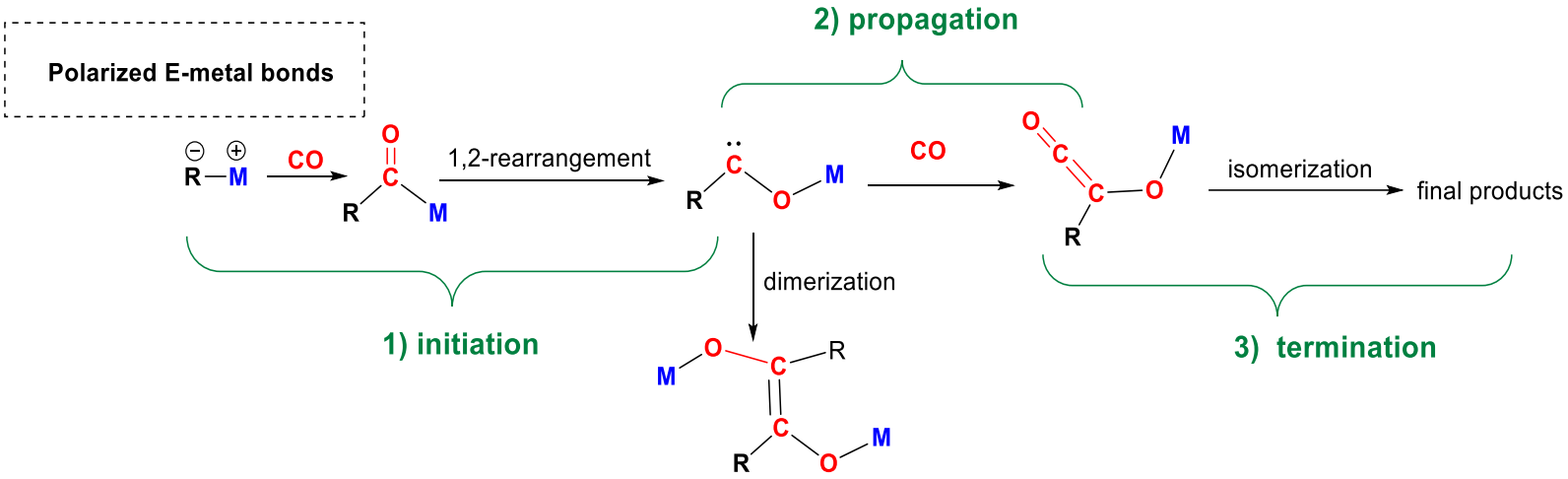
Bertrand, G. et al. *J. Am. Chem. Soc.* **2020**, *142*, 18336−18340.

Contents



R—M = Main group compounds contains polarized **E**-metal bonds, **E** can be B, C, N atom



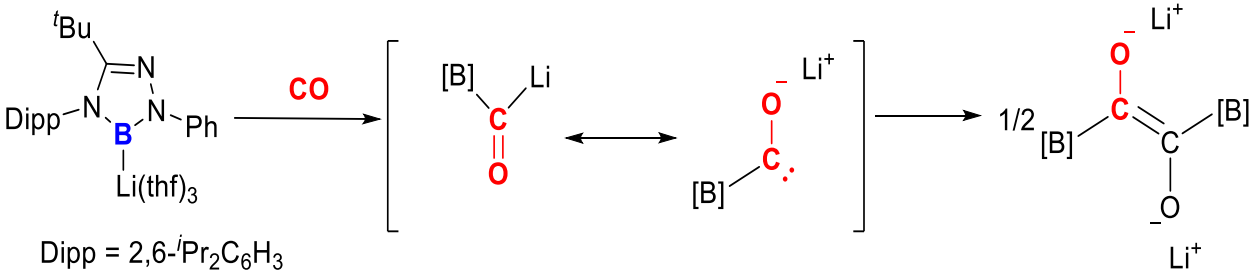


Benzyl potassium / Boryl lithium / Amino lithium

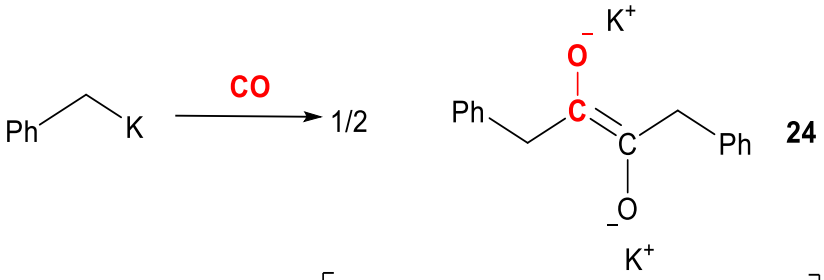
$C_2O_2^{2-}$

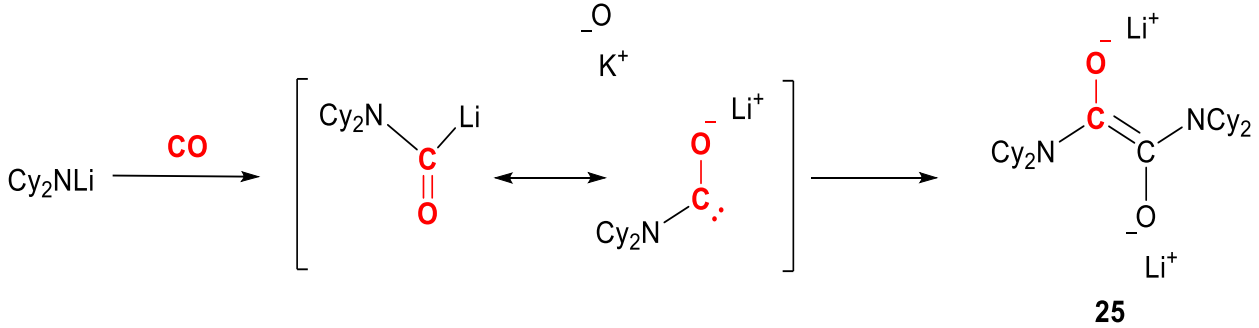
1) initiation: insertion of CO

2) propagation and termination: dimerization of carbene carbon



Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$

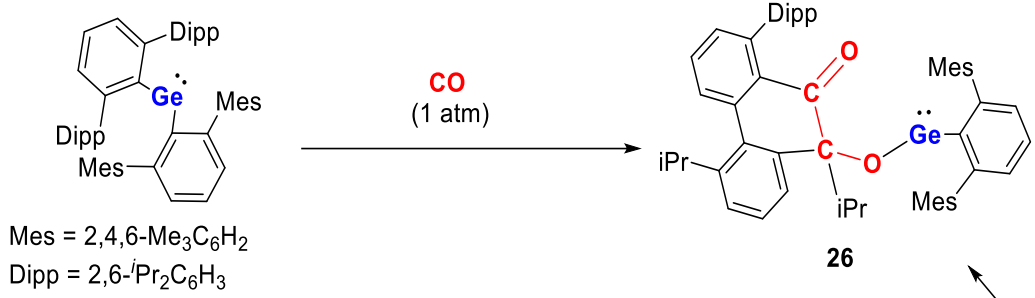




Stephan, D. W. et al. *Chem. Asian J.* **2021**, *16*, 3640−3644.
Stephan, D. W. et al. *J. Am. Chem. Soc.* **2016**,*138*, 6650−6661.
Hou, Z. et al. *J. Am. Chem. Soc.* **2017**, *139*, 16967−16973.

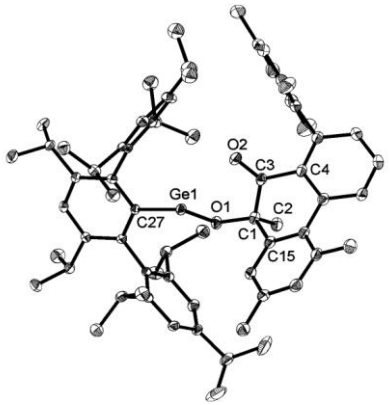
Germylene

1) initiation: insertion of CO
2) propagation: insertion of the second CO
3) termination: insertion of a carbine carbon into a C-C bond of a ligand

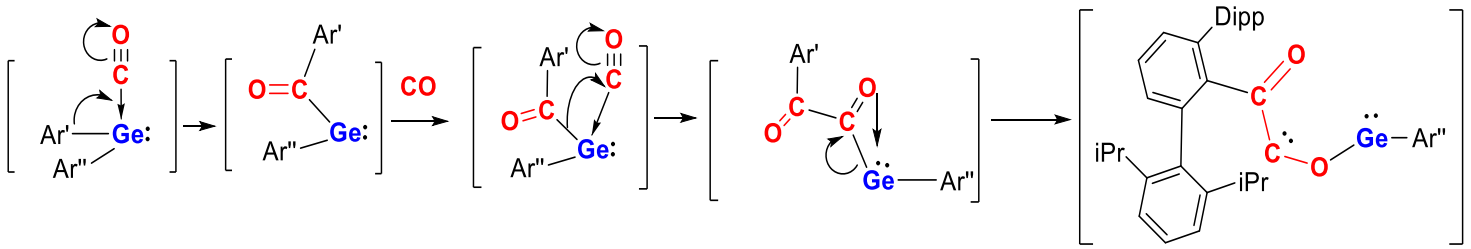


Mes = 2,4,6-$Me_3C_6H_2$
Dipp = 2,6-$^i Pr_2C_6H_3$

26

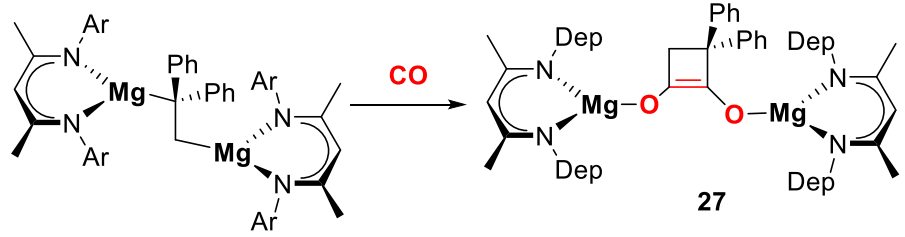


d(free CO) = 1.128 Å
d(C_1-O_1) = 1.403(3) Å
d(C_3-O_2) = 1.214(3) Å



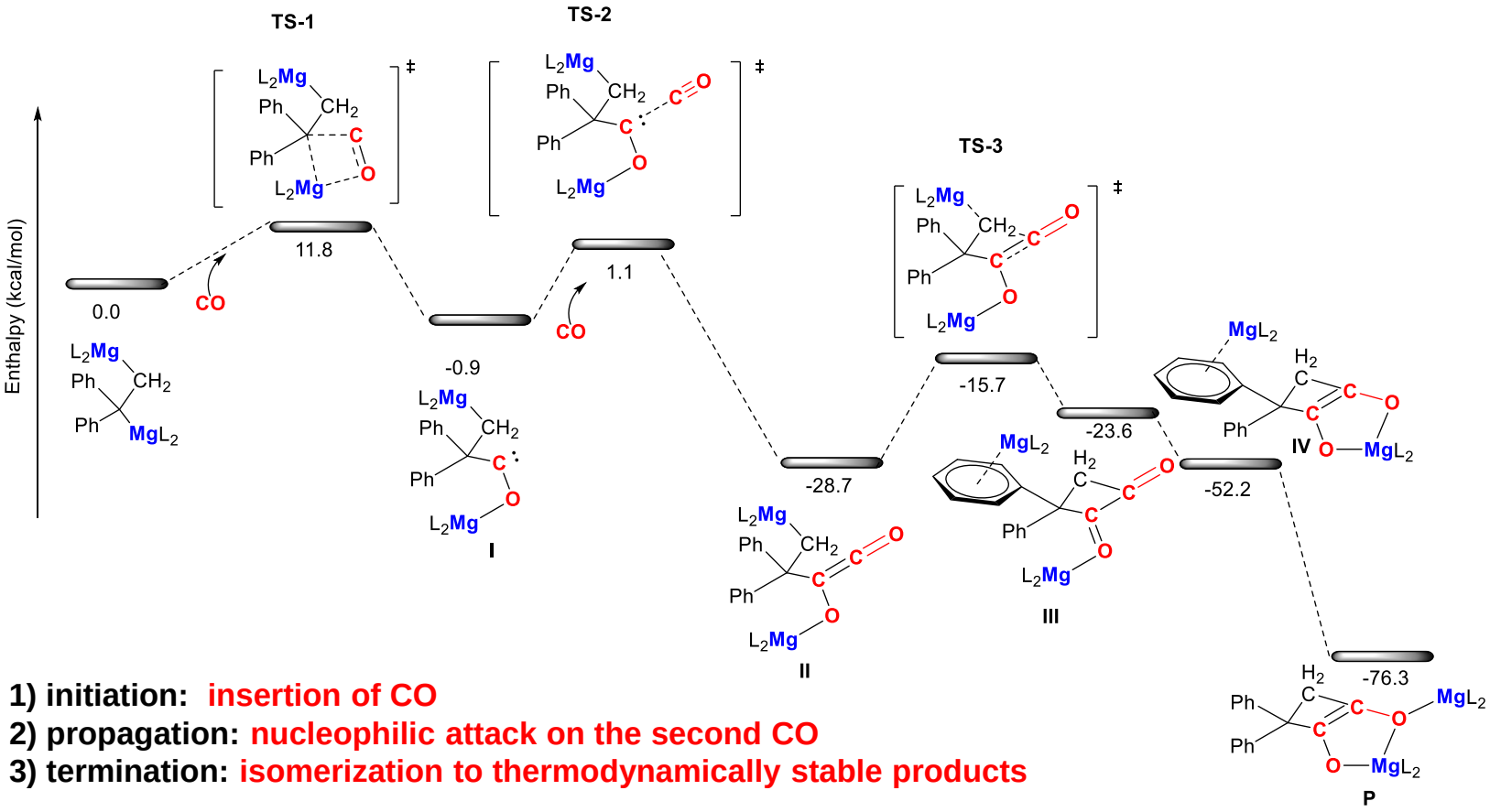
Power, P.P. et al. *J. Am. Chem. Soc.* **2009**, *131*, 6912−6913.

Alkyl Mg dimer



27

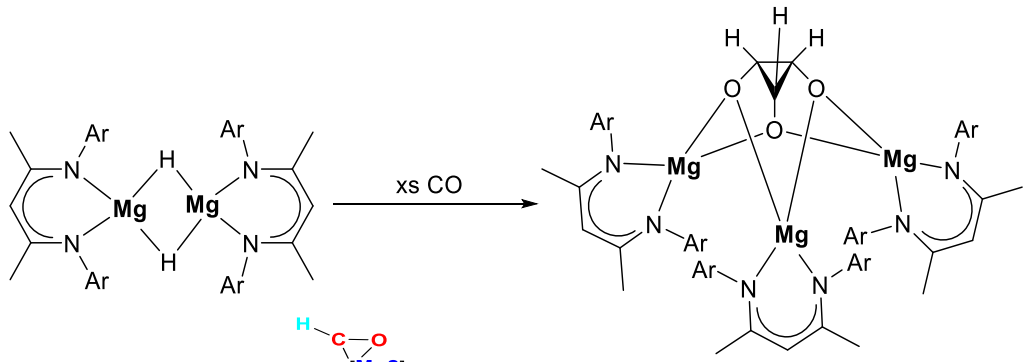
d(free CO) = 1.128 Å
d(O−C) = 1.331 ~ 1.414 Å
d(C−C) = 1.333(2) Å



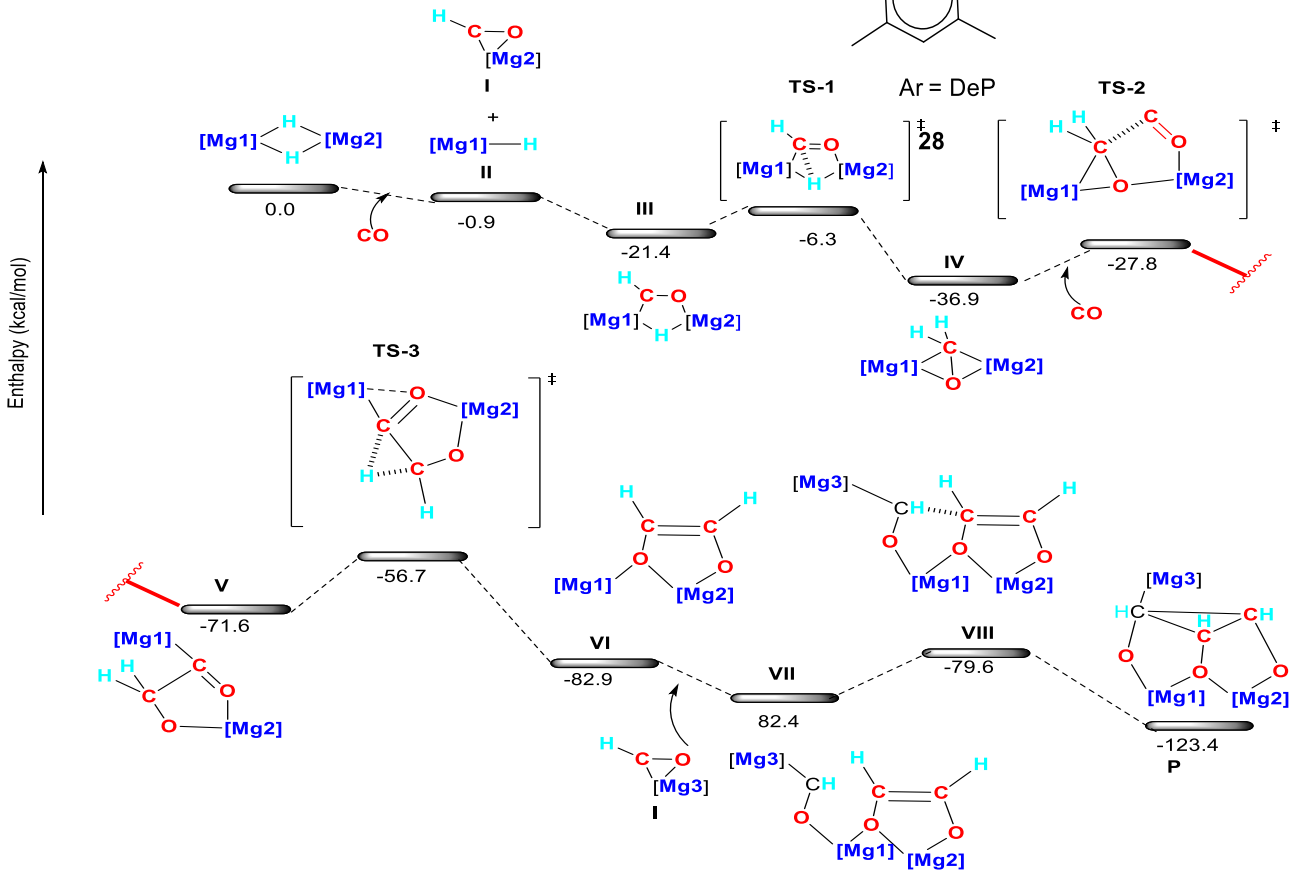
1) initiation: insertion of CO
2) propagation: nucleophilic attack on the second CO
3) termination: isomerization to thermodynamically stable products

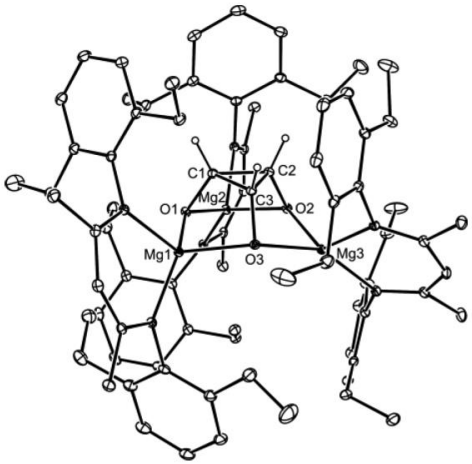
Jones, C. et al. *J. Am. Chem. Soc.* **2015**, *137*, 8944−8947.

Mg–H dimer



d(free CO) = 1.128 Å
d(C−C) = 1.526-1.532 Å
d(C−O) = 1.400(2)−1.411(2) Å

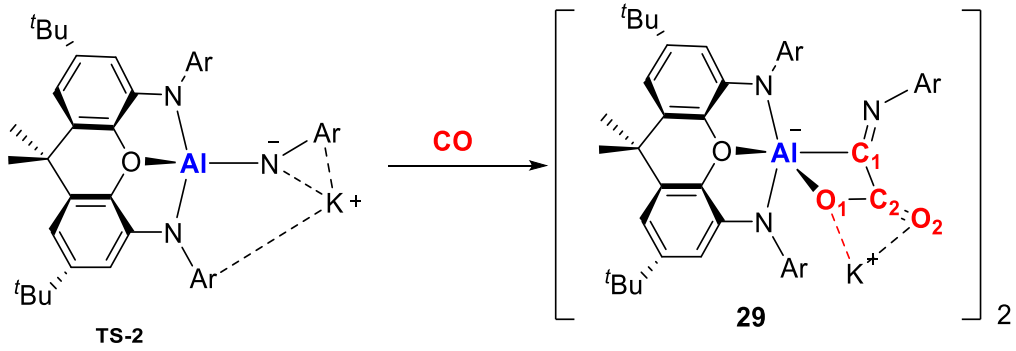




Jones, C. et al. *J. Am. Chem. Soc.* **2015**, *137*, 8944−8947.

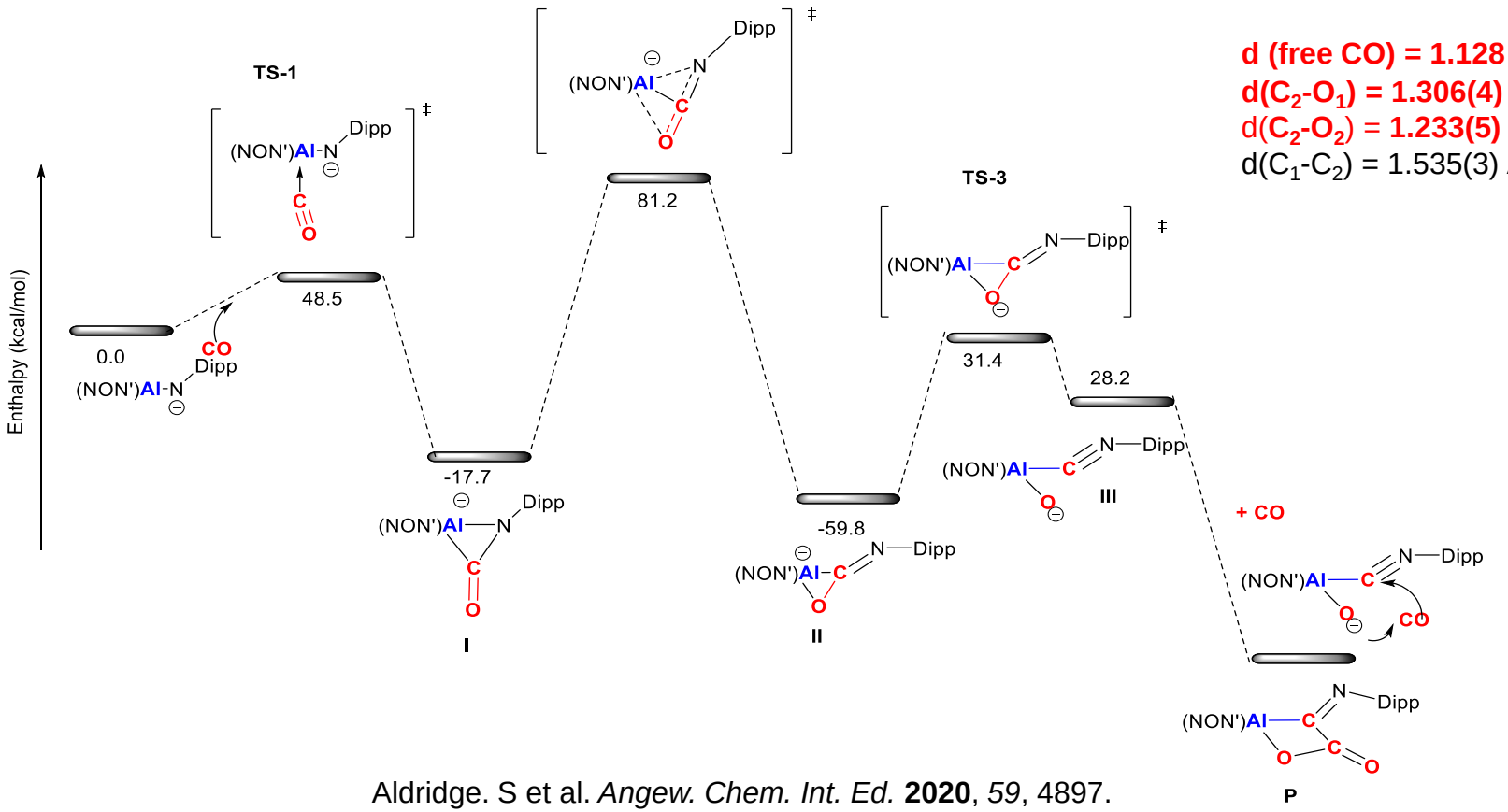
Aluminium imide

1) initiation: insertion of CO
2) propagation and termination:
nucleophilic attack on the second CO



TS-2

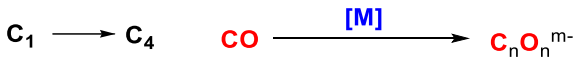
29



d (free CO) = 1.128 Å
$d(C_2\text{-}O_1)$ = 1.306(4) Å
$d(C_2\text{-}O_2)$ = 1.233(5) Å
$d(C_1\text{-}C_2)$ = 1.535(3) Å

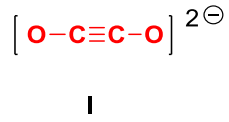
Aldridge. S et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 4897.

Contents

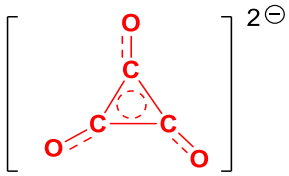


[M] = low valennt main group compounds

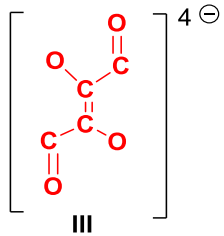
[M] = low valennt main group compounds



I

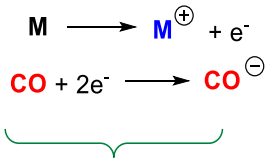


II

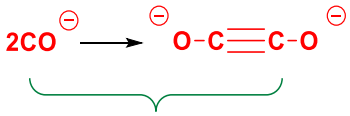


III

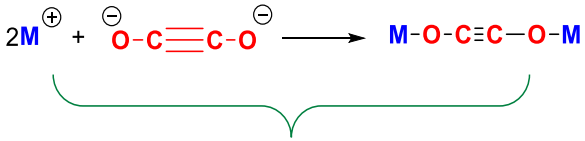
Low valent main group elements



1) initiation



2) propagation

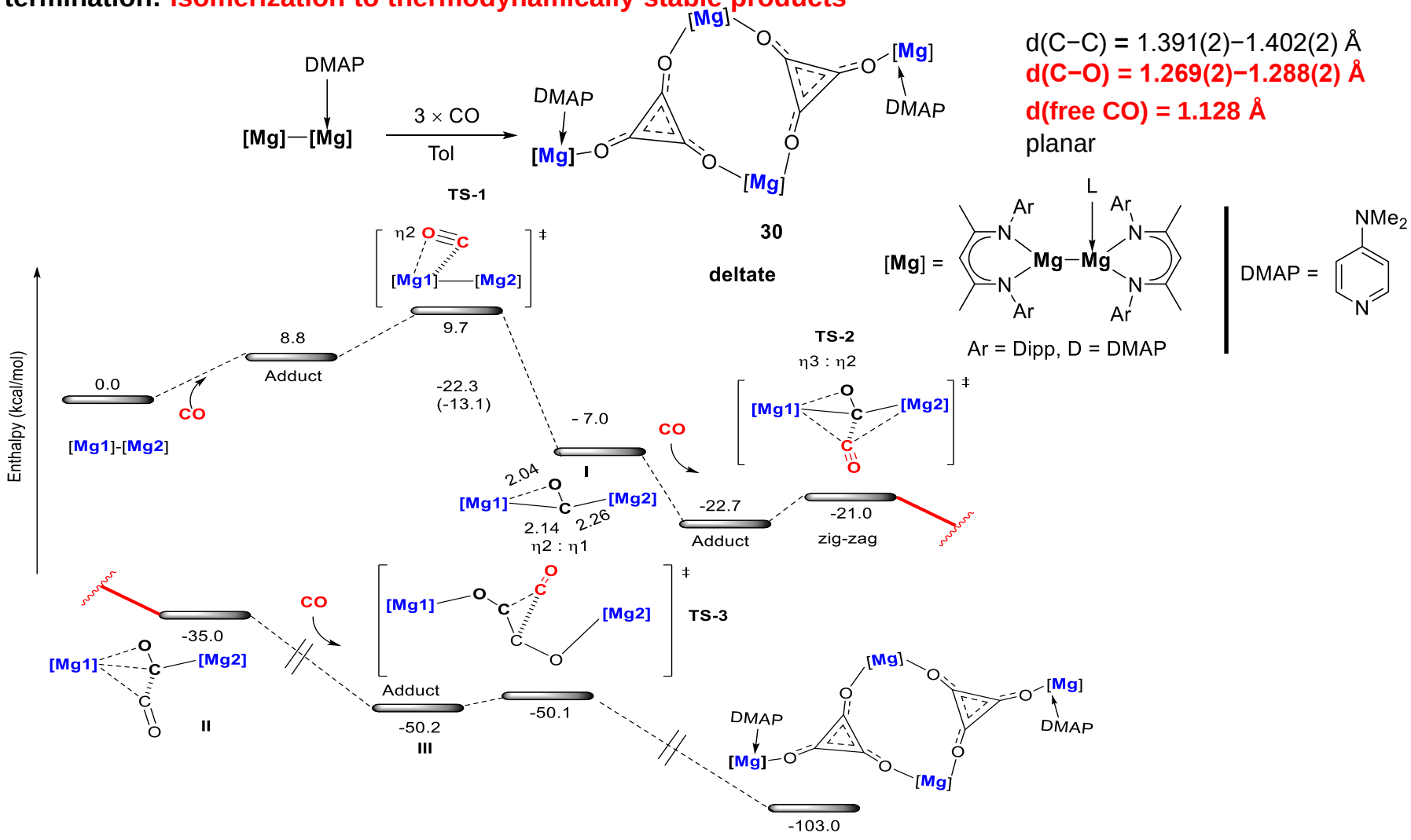


3) termination

Mathew, D. A. et al. *Chem, Commun.*, **2022**, *58*, 5833–5836.

Mg–Mg bond system

1) initiation: insertion of CO
2) propagation: nucleophilic attack on the second CO, insertion of the third CO into Mg-C bond
3) termination: isomerization to thermodynamically stable products



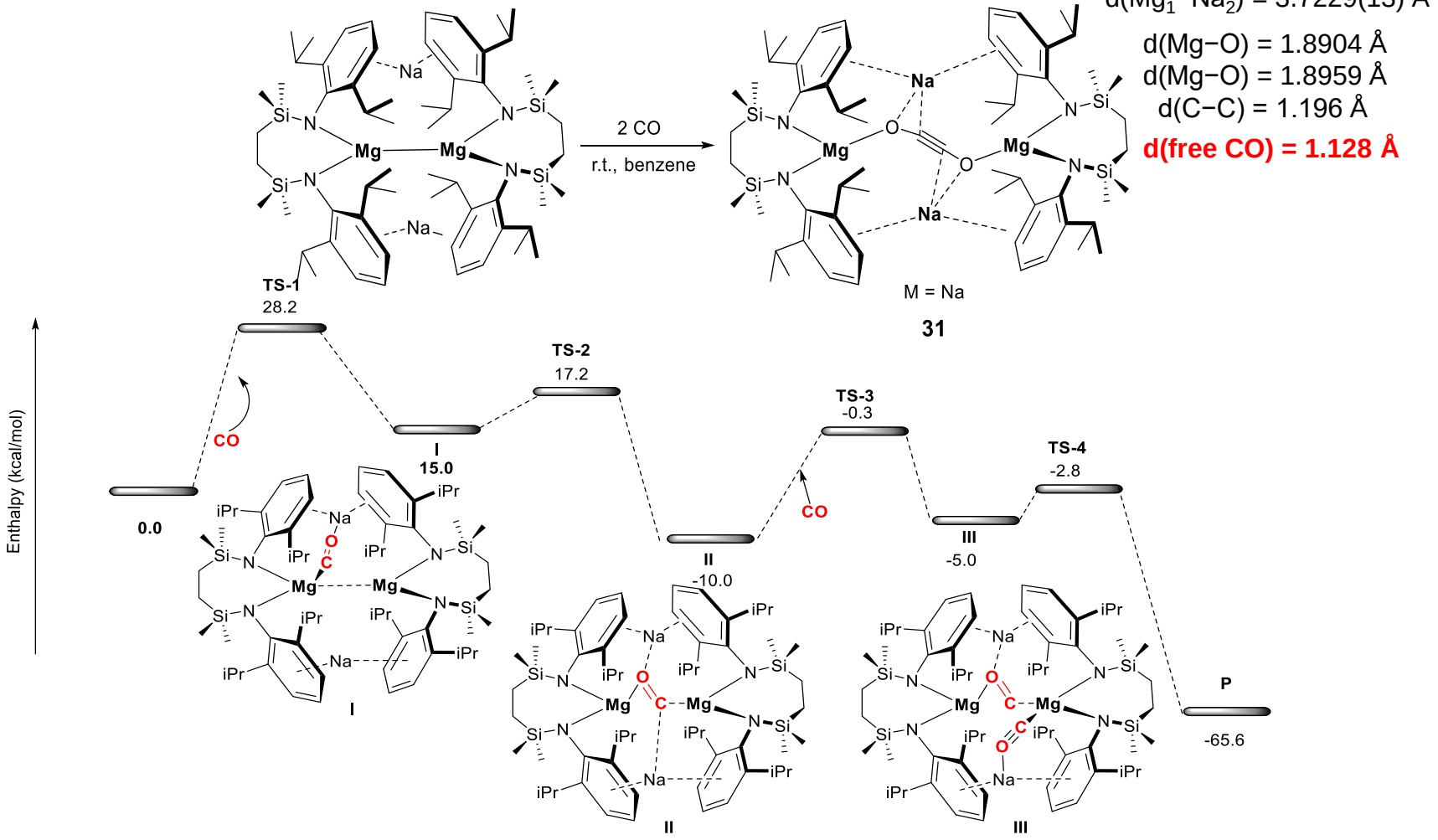
Jones, C. et al. *J. Am. Chem. Soc.* **2019**, *141*, 8764−8768.

Mg–Mg bond system

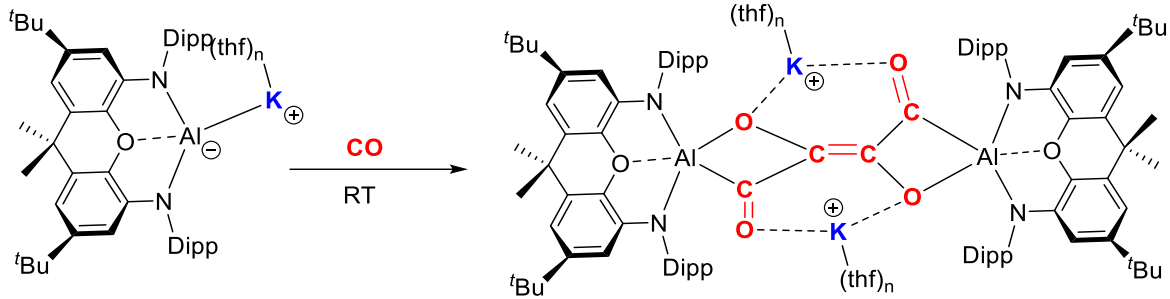
1) initiation: insertion of CO
2) propagation: nucleophilic attack on the second CO
3) termination: isomerization to thermodynamically stable products

$d(Mg_1–Mg_2)$ = 3.2077(10) Å
$d(Mg_1–Na_2)$ = 3.7229(13) Å

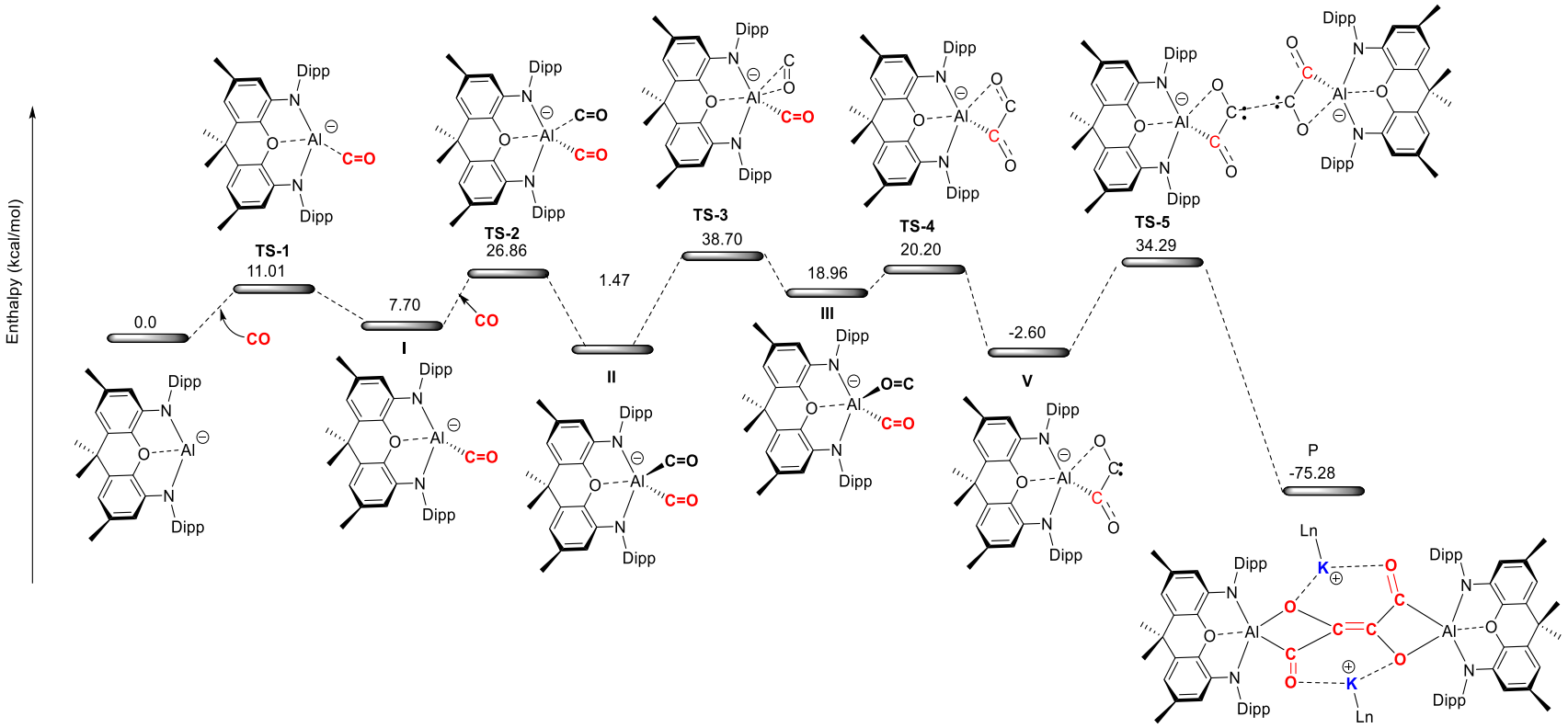
d(Mg–O) = 1.8904 Å
d(Mg–O) = 1.8959 Å
d(C–C) = 1.196 Å
d(free CO) = 1.128 Å



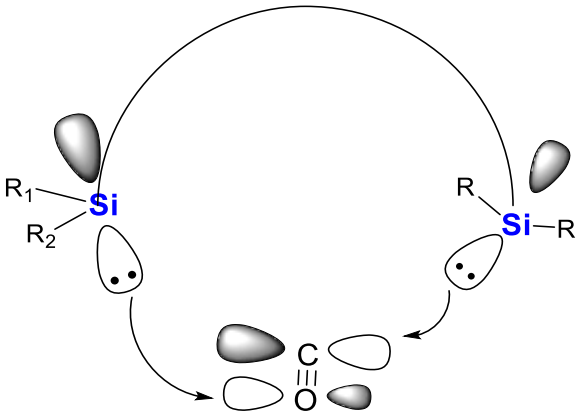
McMullin. C.L., et al. *J. Am. Chem. Soc.* **2021**, *143*, 17851−17856.

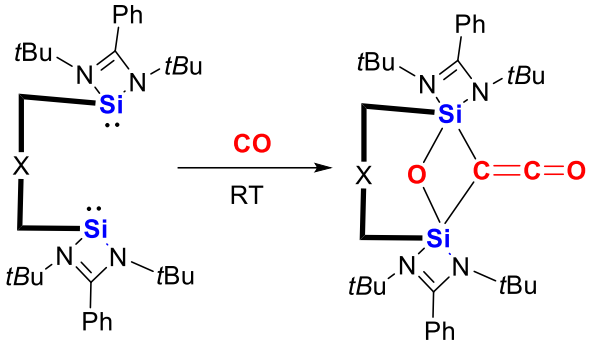


32

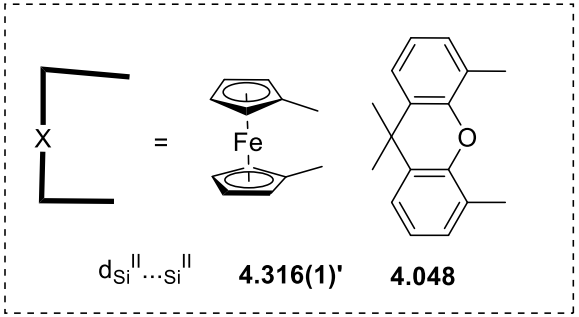


Aldridge. S. et al. *J. Am. Chem. Soc.* **2022**, *144*, 12942−12953.



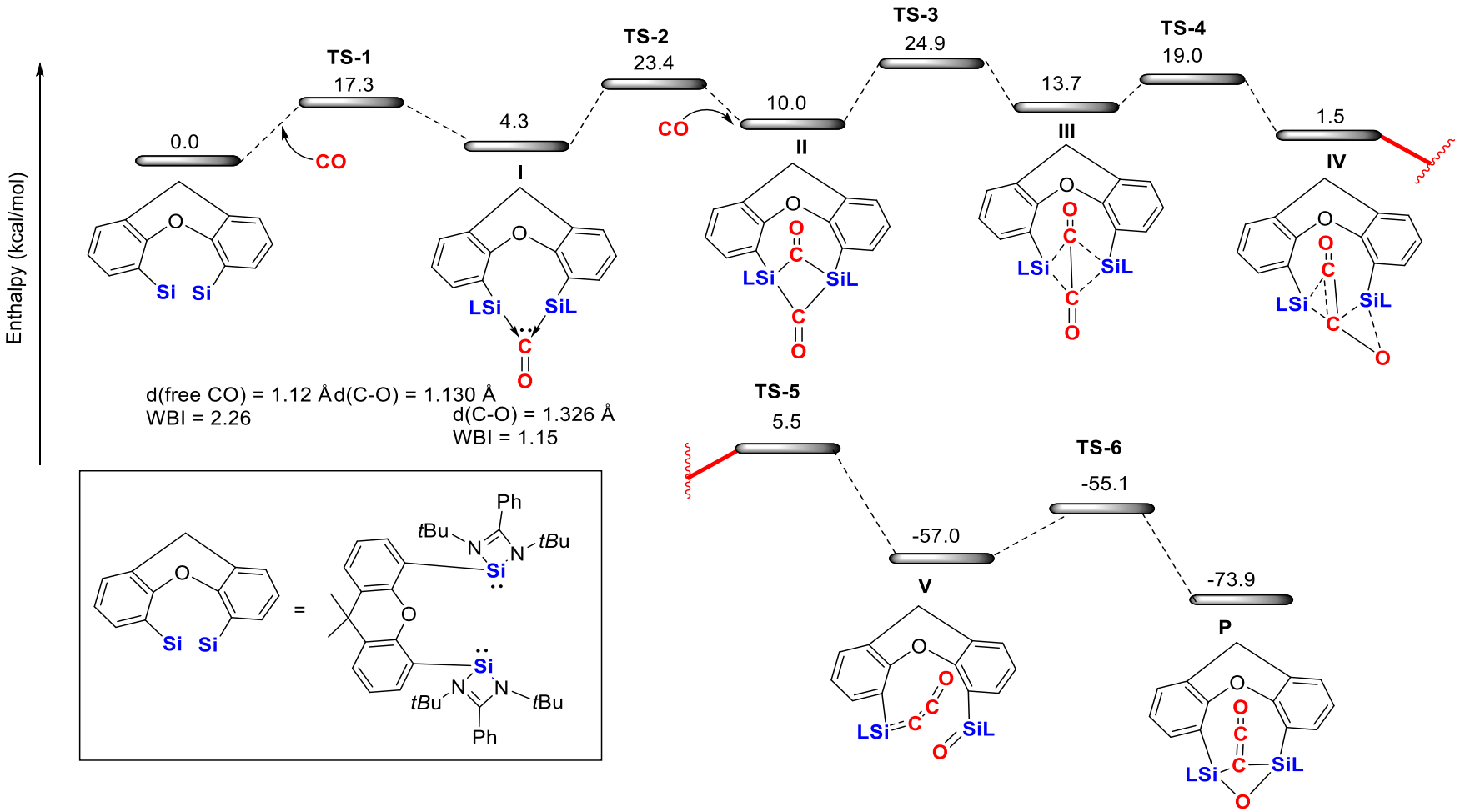


33



Driess, M.et al. *J. Am. Chem. Soc.* **2019**, *141*, 626−634.
Driess, M. et al. *Chem. Commun*. **2020**, *56*, 747−750.

1) initiation: coordination of silylene to two CO, CO as lewis acid
2) propagation: two CO coupled
3) termination: isomerization to thermodynamically stable products

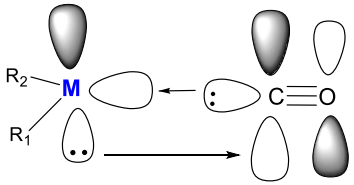


Jones, C. et al. *J. Am. Chem. Soc.* **2015**, *137*, 8944−8947.

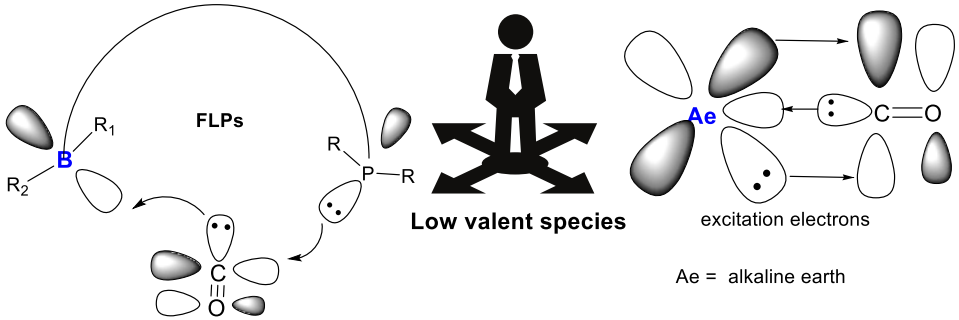
Contents

Summary

Coordination reaction

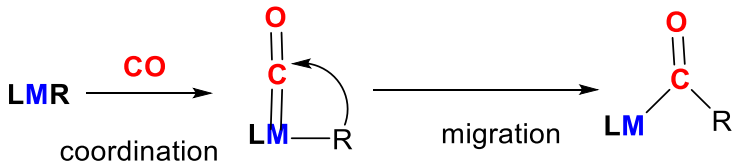


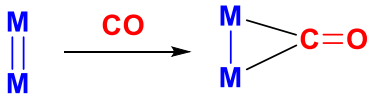
M = main group elements

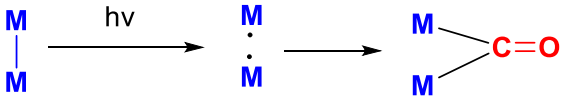


Ae = alkaline earth

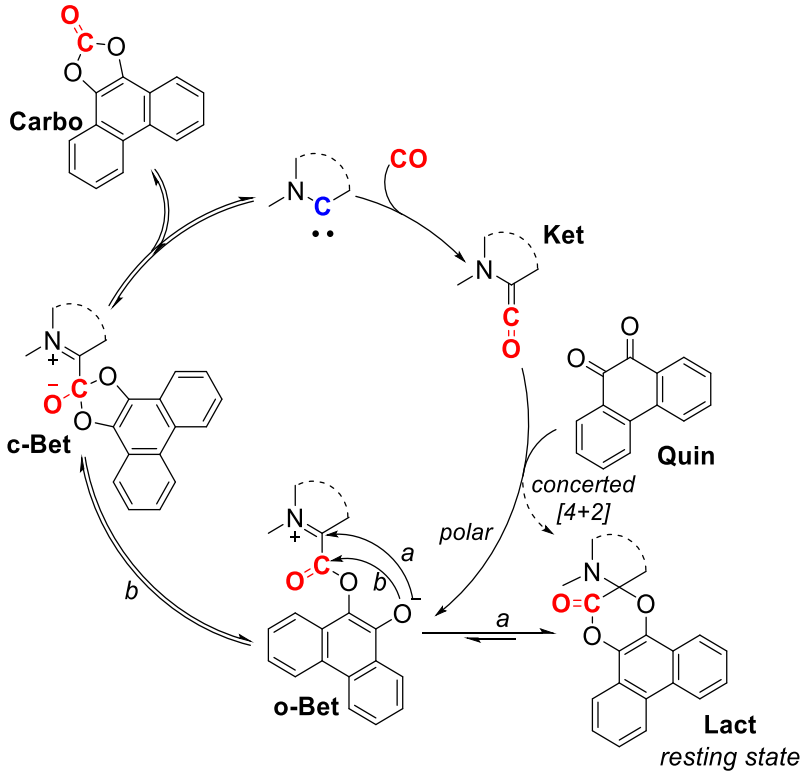
Insertion reaction





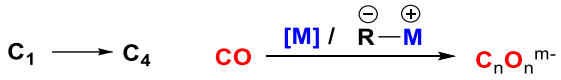


Catalytic reaction

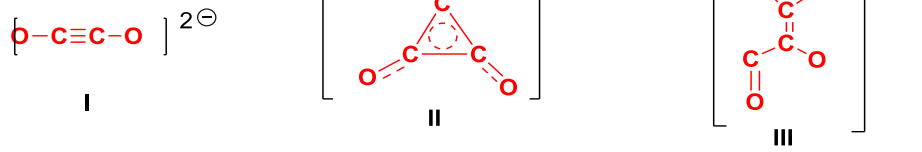


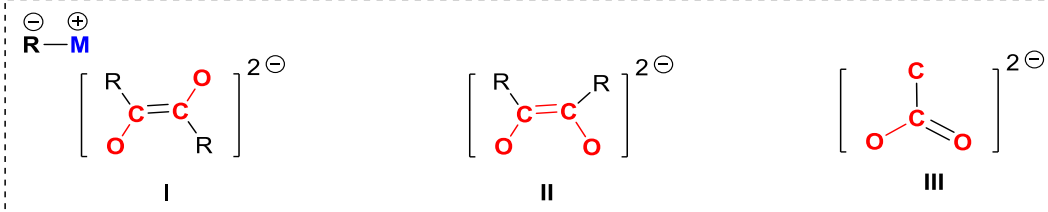
Summary

Reduction coupling reaction



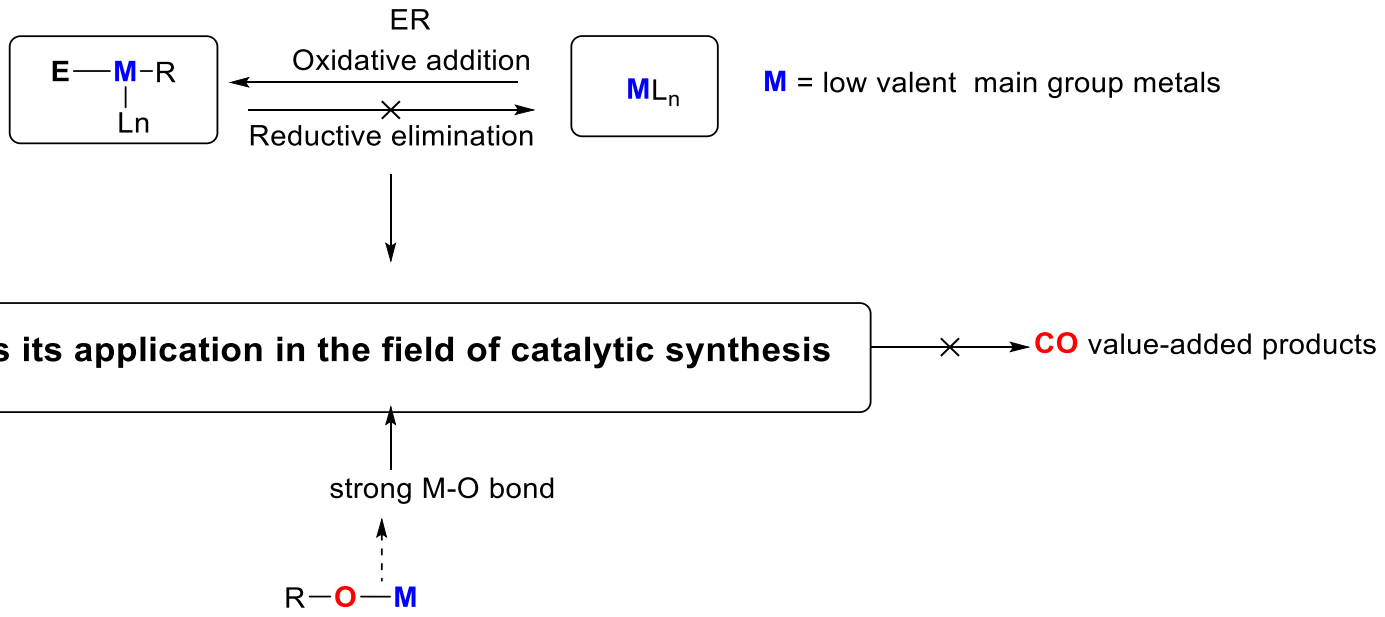
[M] = low valennt main group compounds



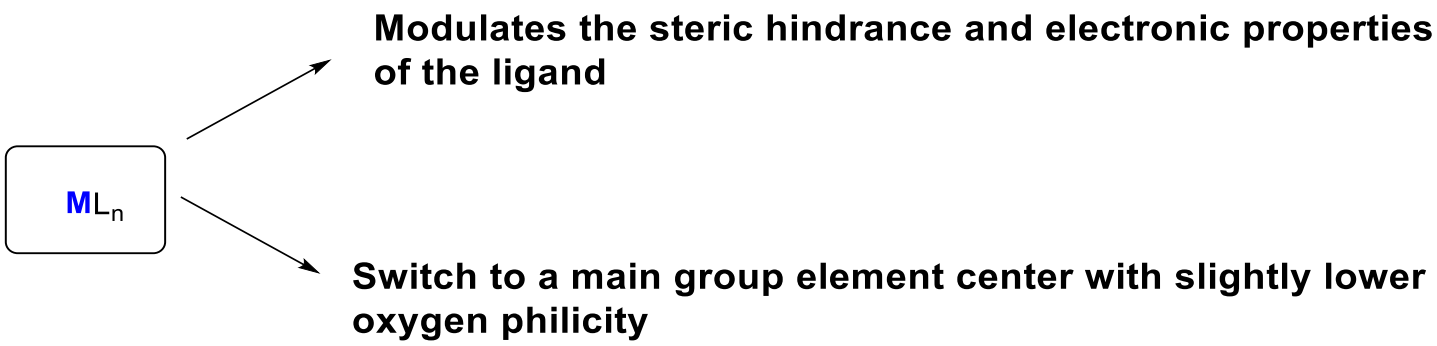


Outlook

Dilemma



Outlook



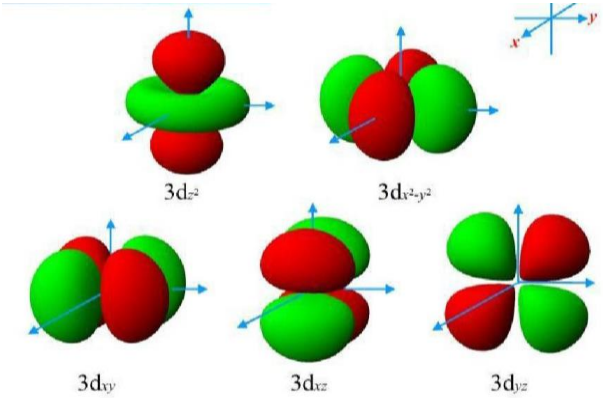
Thank you!

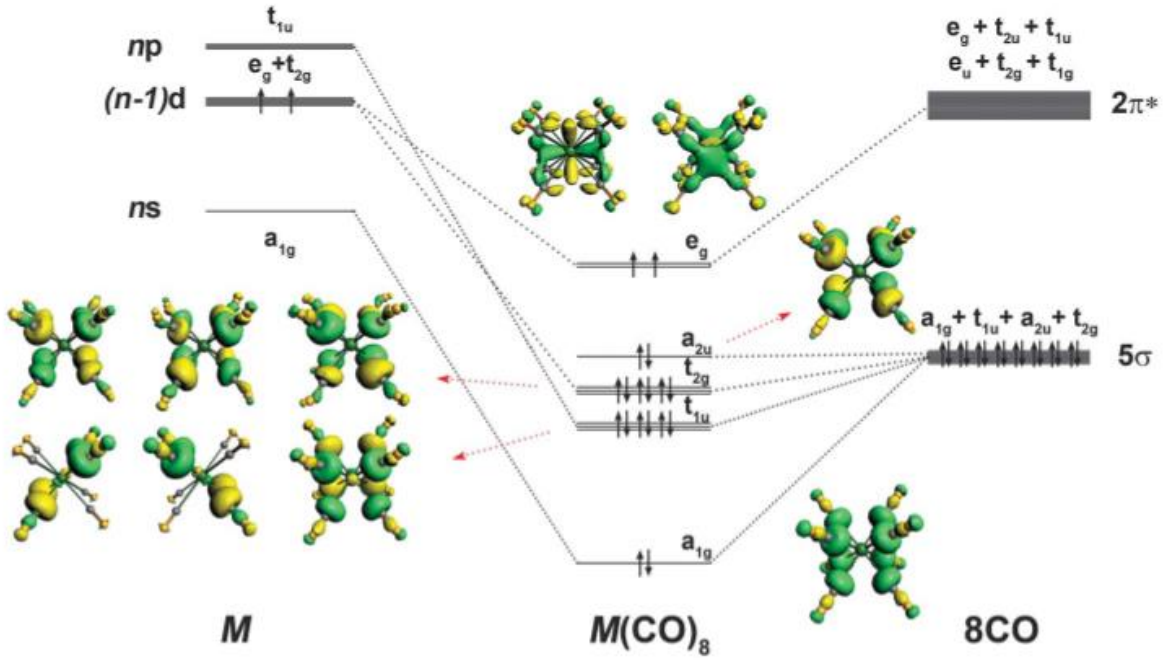
Supplement

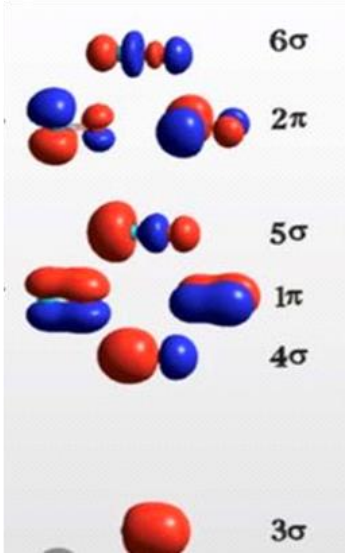
$M(CO)_8$

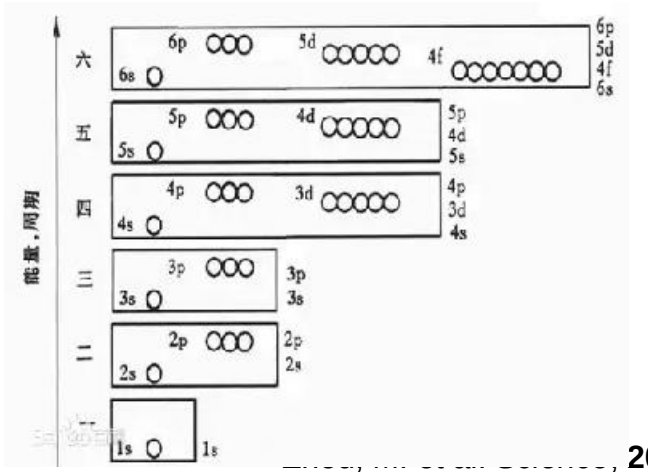
$M(CO)_8$

M = Ca, Sr, Ba



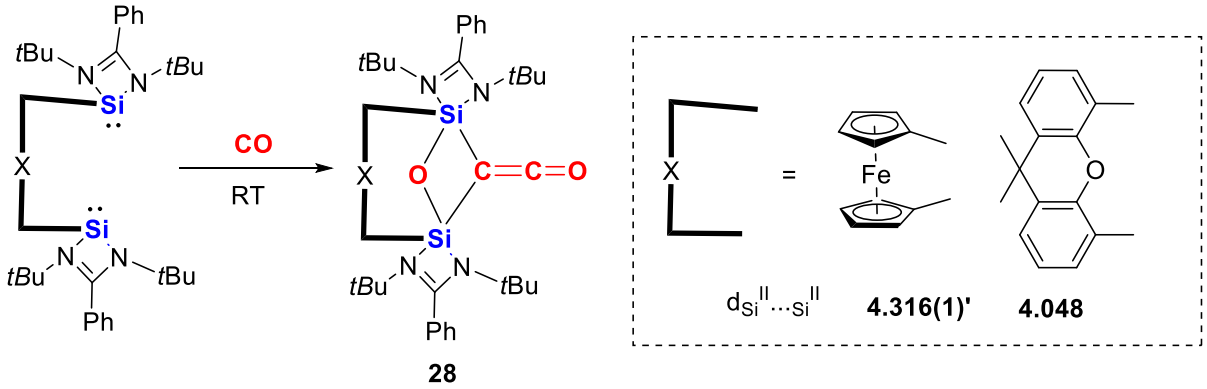


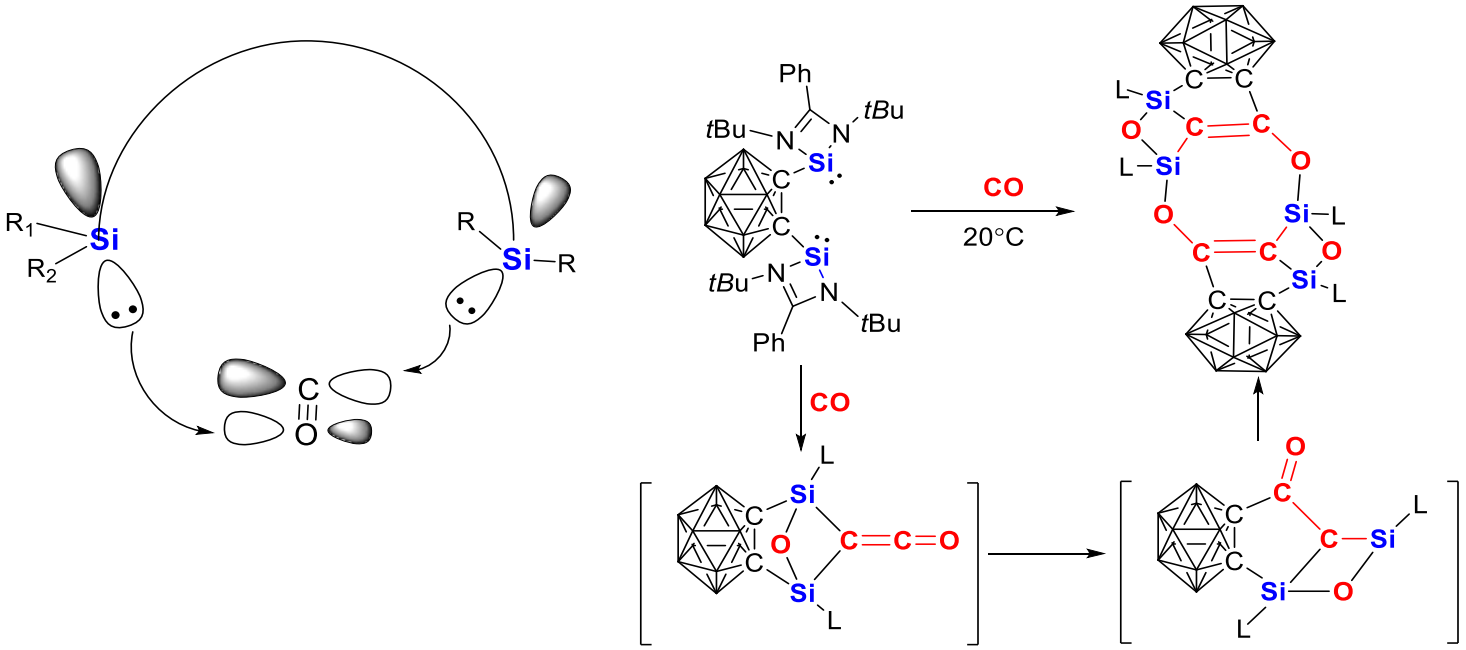




2018, *361*, 912–916.

Synthesis of Silicon Carbonyl Complexes

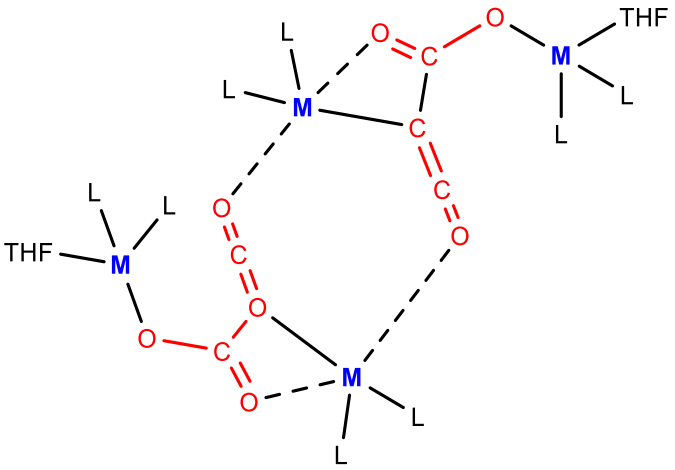


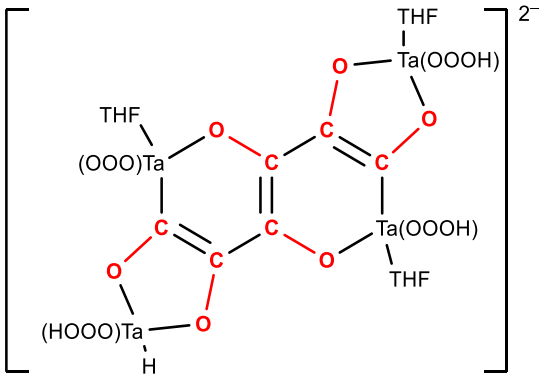


Driess, M.et al. *J. Am. Chem. Soc.* **2019**, *141*, 626−634.
Driess, M. et al. *Chem. Commun*. **2020**, *56*,747−750.

Background

Coupling of CO by early transition metals

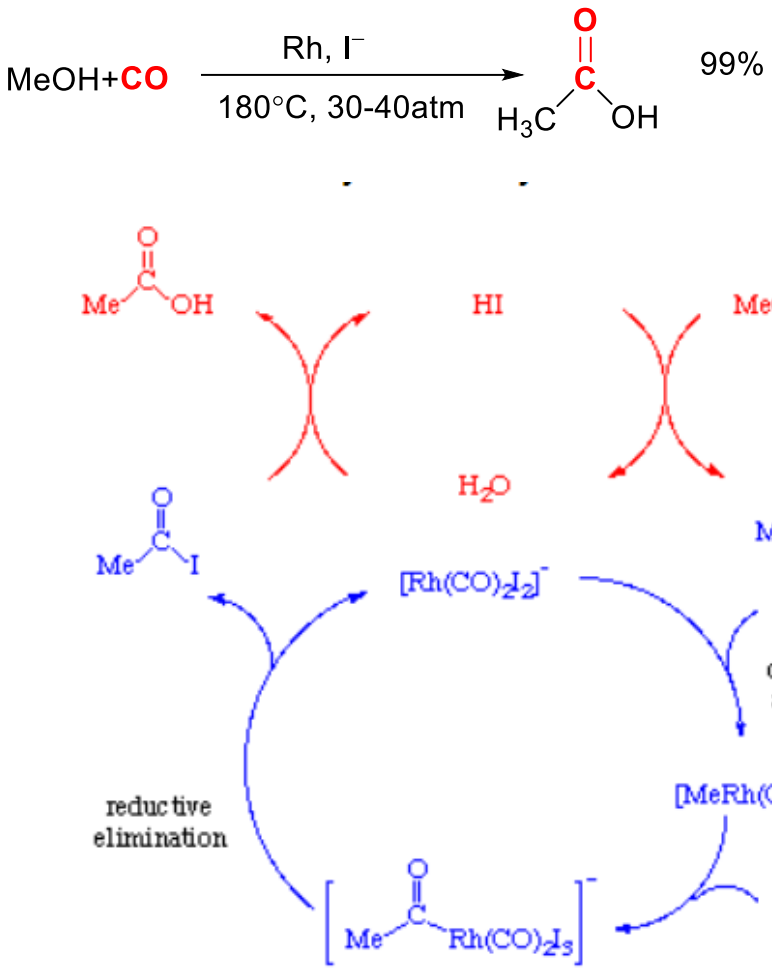




Wu, X.-F. et al.. Transition Metal Catalyzed Carbonylation Reactions, Springer: Germany, **2013**, pp1-234.

Background

Monsanto Acetic Acid Process



Almost any source of Rh and I- will work in this reaction as they will be converted to the actual catalyst.

The role of iodide is simply to promote the conversion of methanol to **methyl iodide**, the species which then undergoes reaction with the **Rh** metal catalyst: