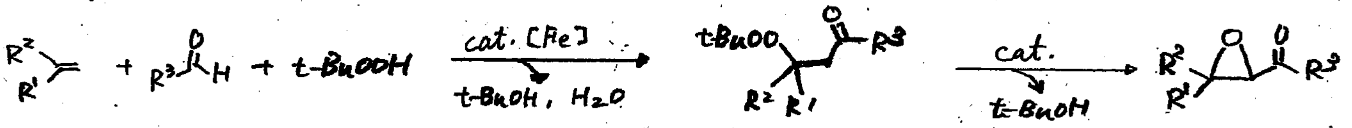
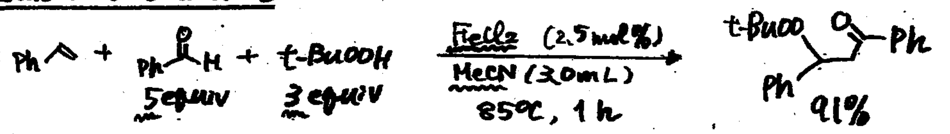
Iron-Catalyzed Carbonylation–Peroxidation of Alkenes with Aldehydes with Hydroperoxides

Ziping Li et al., Renmin Univ. China JACS, 2011. DOI: ja204226n (7+)



Optimization of Conditions

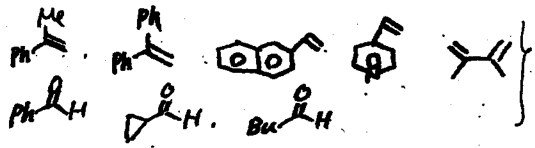


regiochemistry は t-BuOO– がベンジル位

- モル比 … いろいろ
- cat … $FeCl_2$, $FeCl_3$, $FeBr_2$, $Fe(OAc)_2$, $Fe(acac)_2$
- solv. … MeCN, DCE, PhMe, DMSO, H_2O

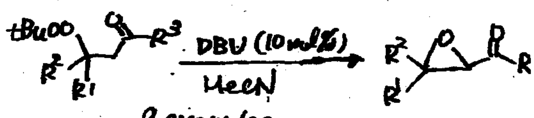
Scope

alkene:
aldehyde:



の組み合せ 15 examples 41~93%

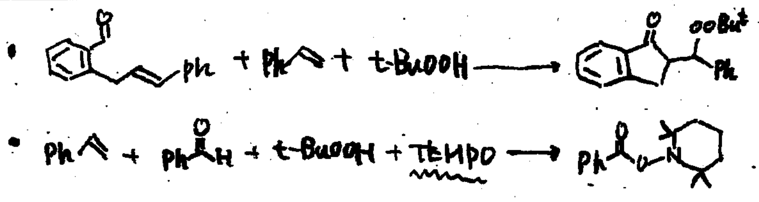
Epoxidation



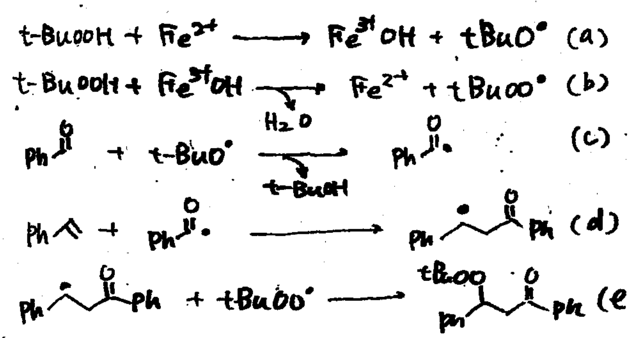
9 examples 78~98%

付加とエポキシ化は one-pot も OK

Mechanism



ラジカル



CT 1702

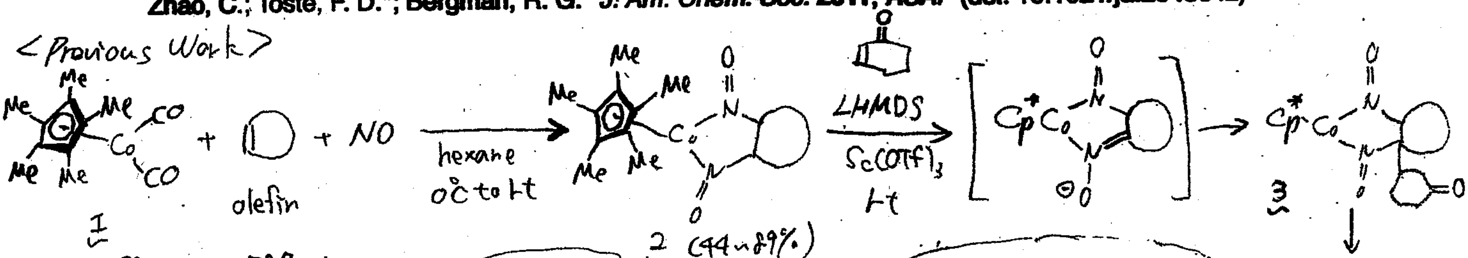
LHMDS ≡ $Li-N(SiMe_3)_2$

Youhei Takeda

"Direct Michael Addition of Alkenes via a Cobalt-Dinitrosyl Mediated Vinylic C–H Functionalization Reaction"

Zhao, C.; Toste, F. D.*; Bergman, R. G.* *J. Am. Chem. Soc.* **2011**, *ASAP* (doi: 10.1021/ja.204564z)

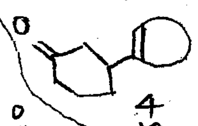
<Previous Work>



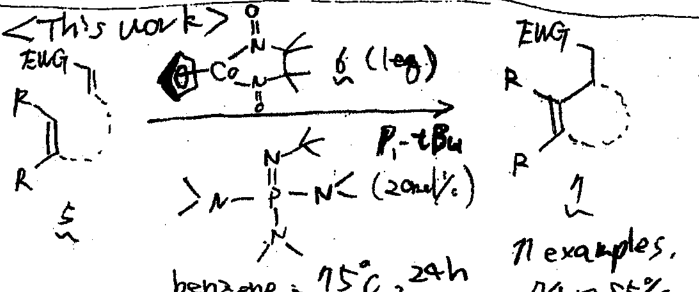
OM, 1983, 2, 787.
JACS, 2008, 130, 3777.

※Ligand と alkene の相互作用

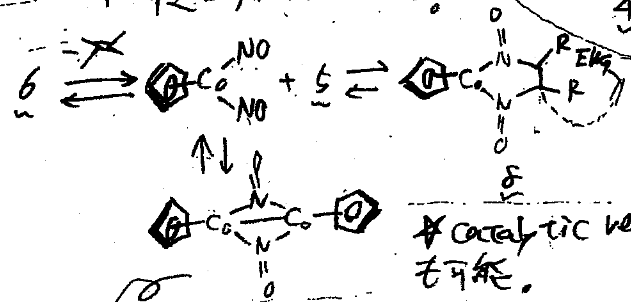
※75℃で 6 はアルケンに可逆的に付加している。



<This work>

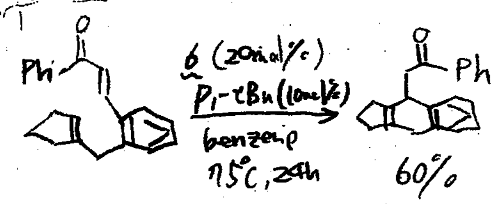


11 examples, 74~85%



安定かつ不活性な錯体 (反応終了時の姿?!)

※catalytic version も可能。



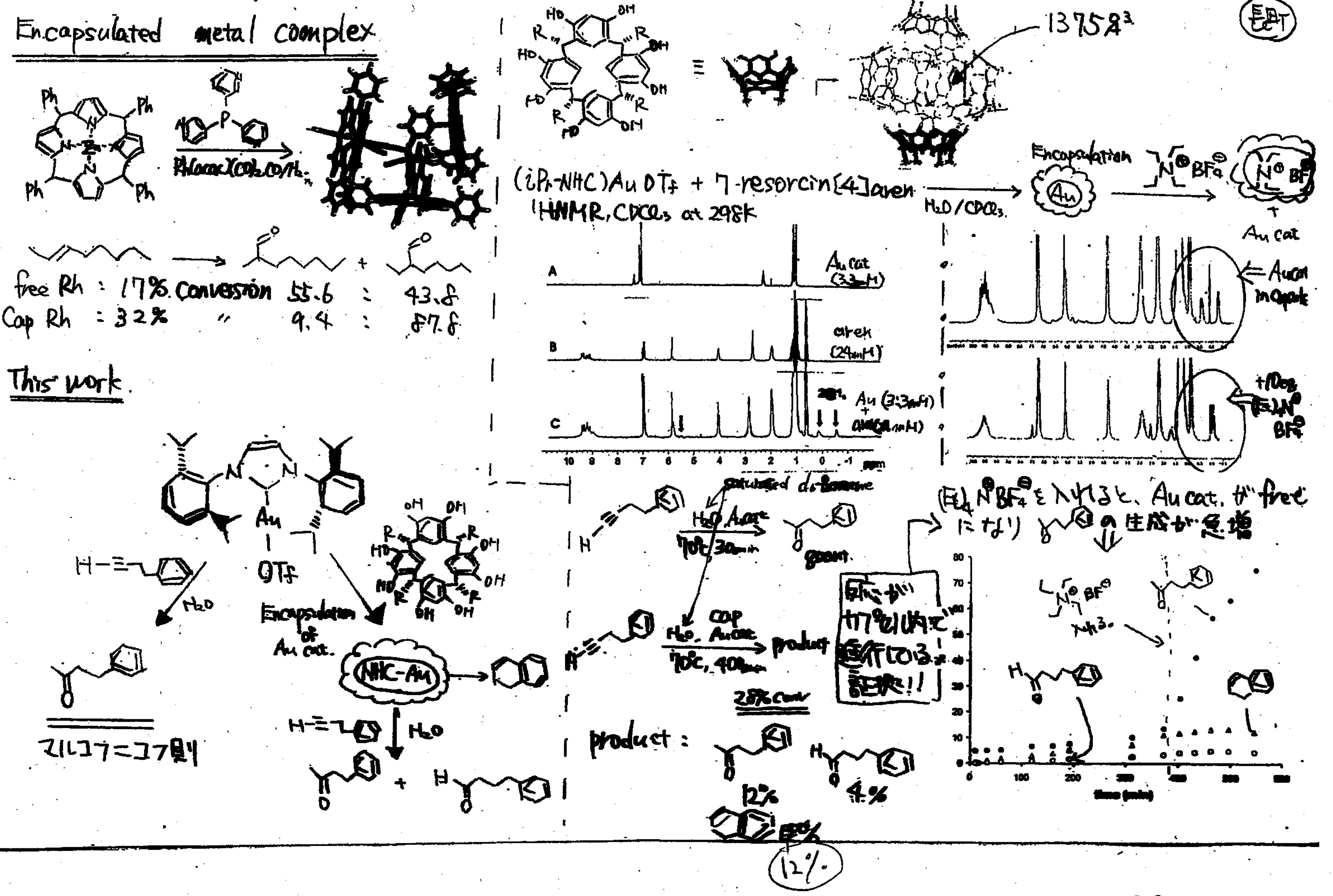
60%

① one-pot で, ① alkene を Mask, ② 分子内 Michael 反応, ③ 脱 Co をおこなった。

◎ 基質適用範囲の拡大。EWG = C(O)Ph 以外に $-CO_2Et$, $-SO_2Ph$, $-NO_2$ 等が利用可。

Supramolecular Control on Chemo- and Regioselectivity via Encapsulation of (NHC)-Au Catalyst within a Hexameric Self-Assembled Host

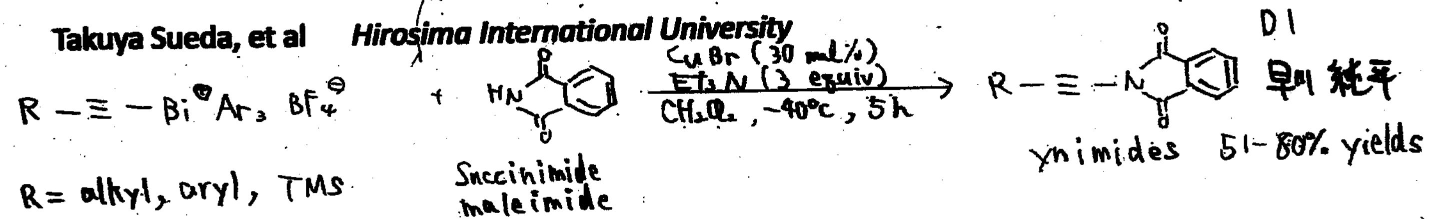
Alessandra Cavarzan,† Alessandro Scarso,*,† Paolo Sgarbossa,‡ Giorgio Strukul,† and Joost N. H. Reek*,§ *J. Am. Chem. Soc.* **2011**, *133*, 2848-2851.

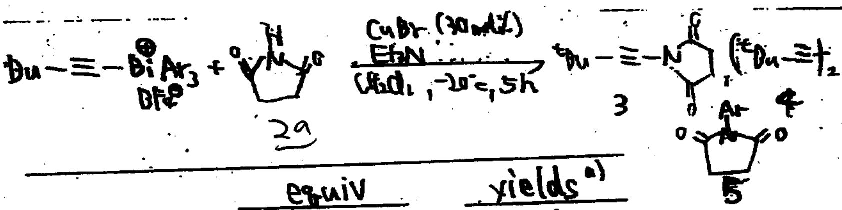


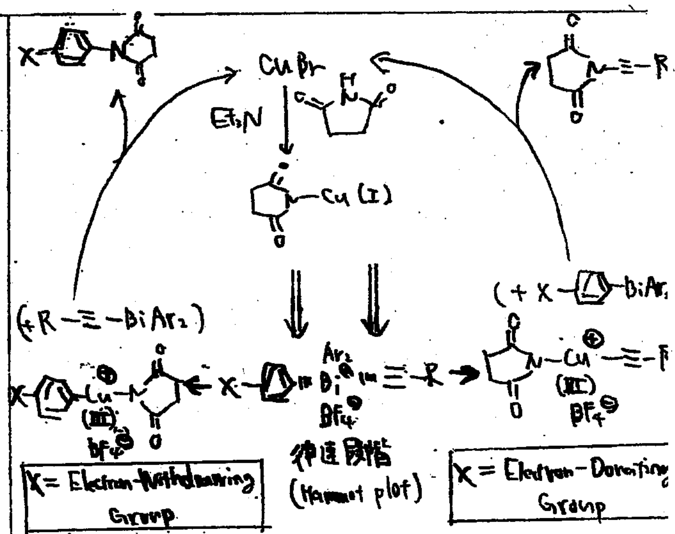
N-Alkynyl Imides (Ynimides): Synthesis and Use as a Variant of Highly Labile Etynamine

Org. Lett. ASAP. DOI: 10.1021/ol2014973

Takuya Sueda, et al *Hirosima International University*

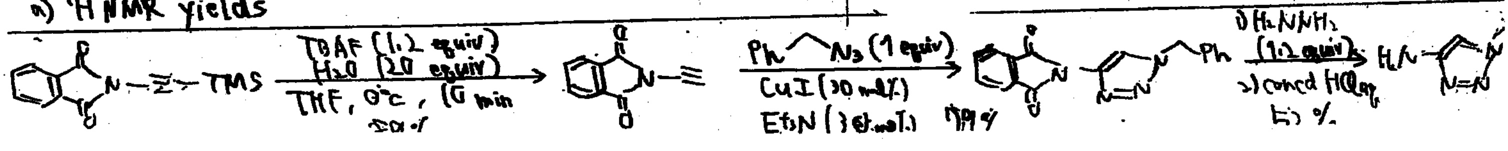






Ar	equiv 2a	equiv Et3N	yields a) 3	4	5
p-MeOC6H4	1	1	54	32	9
p-MeOC6H4	2	2	69	7	19
p-MeOC6H4	3	3	70	10	20
p-MeC6H4	3	3	80	2	18
Ph	1	1	50	22	27
p-ClC6H4	1	1	13	21	66

a) 1H NMR yields

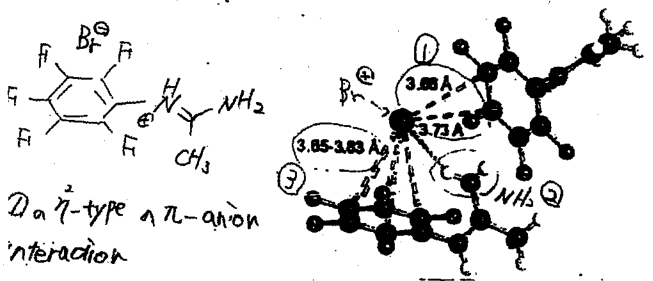


From attraction to repulsion: anion–π interactions between bromide and fluorinated phenyl groups

Giese, M.; Albrecht, M.*; Bannwarth, C.; Raabe, G.; Valkonen, A.; Rissanen, K.*　　M2 奥村 壮太

Chem. Comm. **DOI:** 10.1039/c1cc12667a

Previous Work

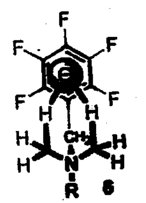


① の η^2-type の π-anion interaction

② と NH_2 との interaction

③ の η^6-type の π-anion interaction

JACS, 2008, 130, 4600.



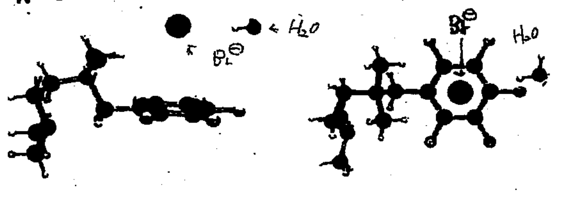
Chem. Eur. J. 2010, 16, 5062

の η^6-type の π-anion interaction

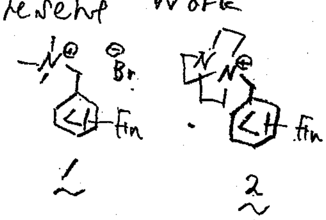
Ph の C と Br のキョリは 3.63～3.83 Å

R = $CH_2CH_2N(CH_3)_2$

結晶は一水和物



Present Work



a F_5
b 2,3,5,6-F
c 2,4,6-F
d 2,6-F

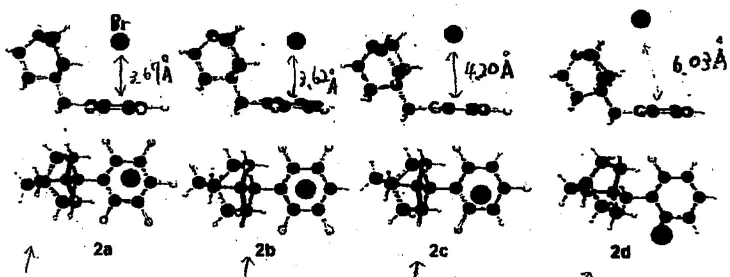
1 のとき、($MP2/6\text{-}311{+}{+}G^{**}$ 計算)

aromatic unit と $Br^{\ominus}$ のキョリ

1a (3.294 Å) < 1b (3.320 Å) < 1c (3.362 Å) < 1d (3.415 Å)

π電子の減少にともなってキョリは短かくなる

2 のとき (X線)



アニリニウム塩のX線でこの位置が…　2aと変化なし　π-anion 作用無し

CT 2011/07/02

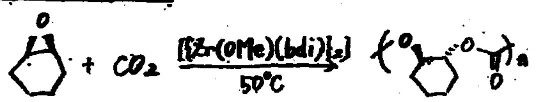
M2 Yuki Mitani

Tetravalent Metal Complexes as a New Family of Catalysts for Copolymerization of Epoxides with Carbon Dioxide

Koji Nakano, Kazuki Kobayashi, and Kyoko Nozaki*

J. Am. Chem. Soc. (DOI: 10.1021/ja203382q)

Previous Work



Coates, G. W. et al. Angew. Chem. Int. Ed. 2002, 41, 2599.

This Work

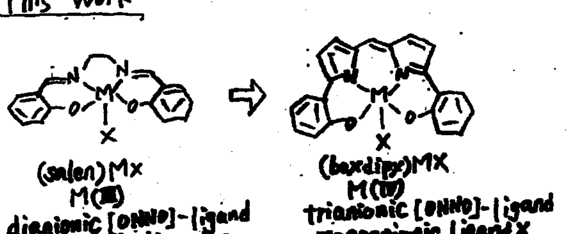


Figure 1. Design strategy for the tetravalent metal complexes.

M = B, Al, Si などの BOXDIPY ligand は最近報告されている。今回、著者らは、M = Ti, Zr, Ge, Sn の BOXDIPY ligand を初めて調製し、これらの錯体を用いて、エポキシドと CO_2 の共重合を報告している。

Scheme 1. Synthesis of (BOXDIPY)MCl Complexes (M = Ti, Zr, Ge and Sn)

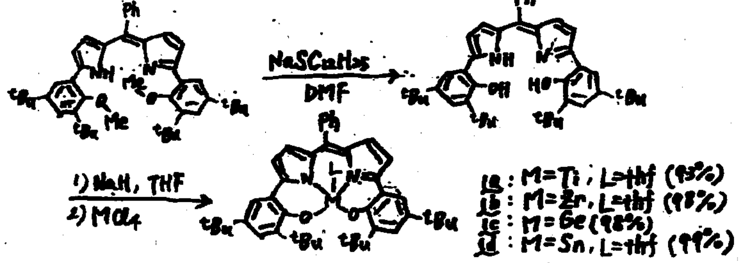
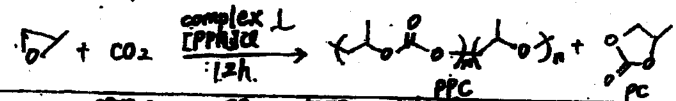


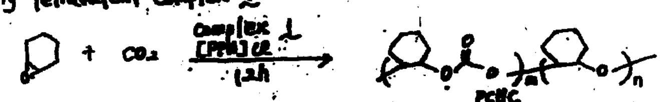
Table 1. Copolymerization of Propylene Oxide with CO_2 by Using Tetravalent Complexes 1



entry	1	[PPN]Cl (equiv to 1)	CO_2 [MPa]	temp [°C]	yield of PPC + PC (%)	PPC/PC
1	1a	1.0	2.0	60	25	71/29
2		1.0	2.0	80	55	33/67
3		1.0	2.0	100	98	2/98
4		0.5	2.0	60	21	82/18
5		1.5	2.0	60	83	1/99
6	1b	1.0	2.0	60	21	0/100
7	1c	1.0	2.0	60	15	71/29
8		1.0	2.0	80	26	40/60
9		1.0	2.0	100	82	0/100
10		0.75	2.0	60	13	93/7
11		0.75	4.0	60	17	93/7

[PPN]Cl : $[Ph_3P{=}N{=}PPh_3]Cl$

Table 2. Copolymerization of Cyclohexene Oxide with CO_2 by Using Tetravalent Complex 1

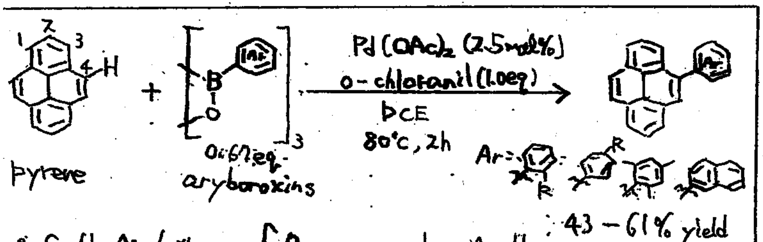


entry	1	yield (%)	TOF for PCHC	PCHC carbonate linkage (%)
1	1a	45	96	99
2	1b	5	8	54
3	1c	36	60	99
4	1d	10	17	75

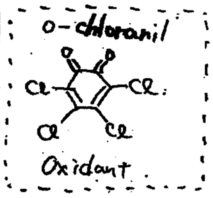
Direct Arylation of Polycyclic Aromatic Hydrocarbons through Palladium Catalysis

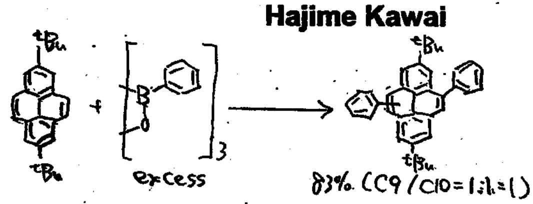
K. Itami *et al.* *J. Am. Chem. Soc.* ASAP

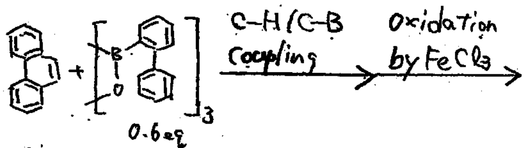
Hajime Kawai

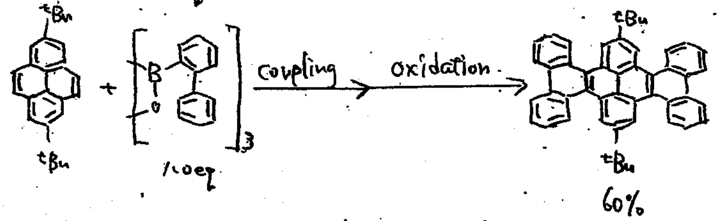


• C-H Arylation of Pyrene with Arylboroxins.
 C4 - selective arylation.

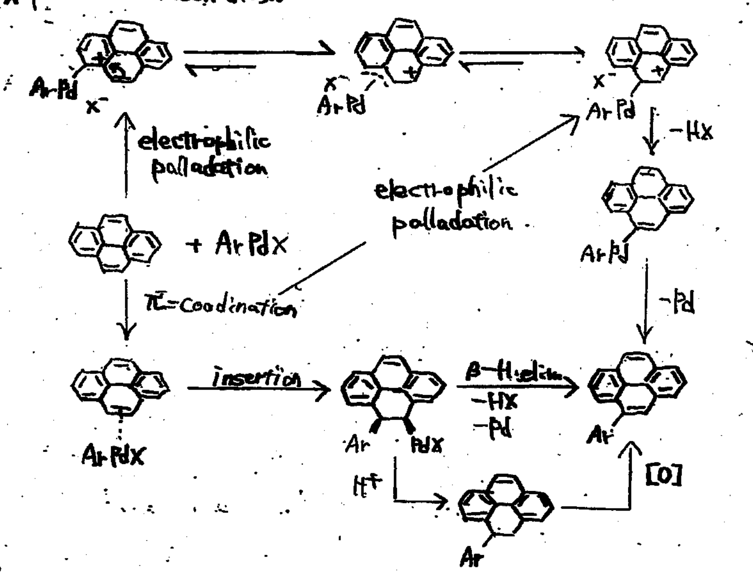






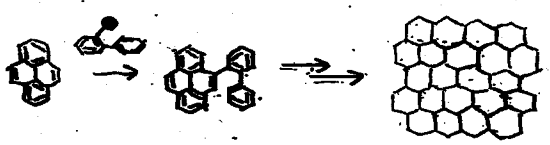


★ possible mechanism



• Sequential C-H Arylation and $FeCl_3$ Oxidation
⇓
extending : PAH (polycyclic aromatic hydrocarbon)

• Future work
 Controlled synthesis of graphenes



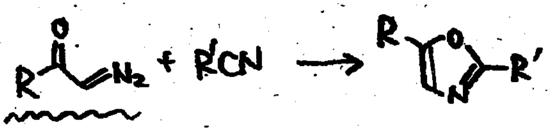
graphene sheet !!

An Efficient [2 + 2 + 1] Synthesis of 2,5-Disubstituted Oxazoles via Gold-Catalyzed Intermolecular Alkyne Oxidation

Yuki Ikeda

He, W.;Li, C.; Zhang, L *JACS*, 2011, 133, 8482-8485.

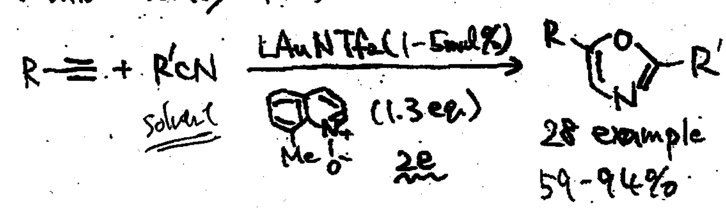
<一般的なオキサゾール合成法>



有害.爆発性
市販されていない

R: ほとんどがAryl

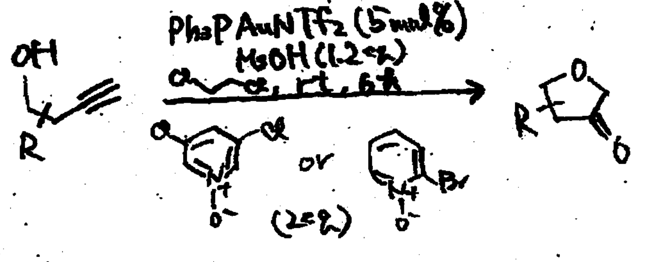
<This Work>



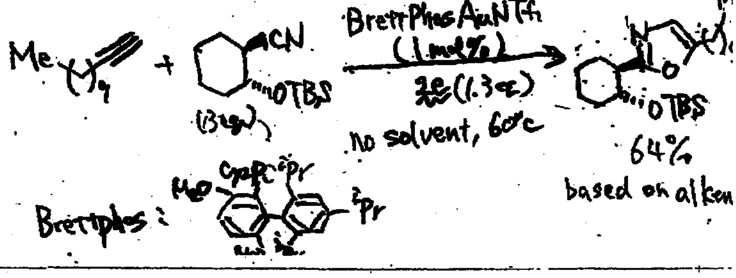
R: $(CH_2)_2Ph$, $(CH_2)_2OH$, $(CH_2)_3OTBS$, $(CH_2)_2OTHP$
 $(CH_2)_2CO_2H$, $(CH_2)_2SPh$, $(CH_2)_4NHBoc$, $(CH_2)_4Cl$
 [ring], [ring], [ring], tBu,
 [ring]R'' (R'': H, 4-OMe, 4-CHO, 2-Me)

R': Me, Et, iPr, Ph

<Previous Work>



When the nitrile is expensive and/or not commercially available

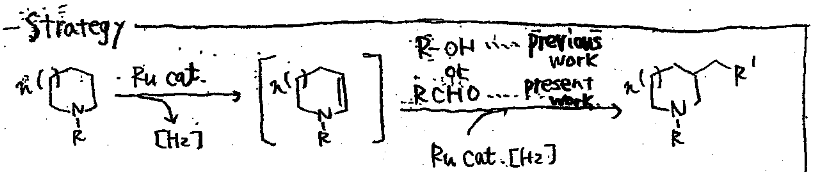


sp^3 C–H Bond Activation with Ruthenium (II) Catalysts and C(3)-Alkylation of Cyclic Amines , M1 [redacted]

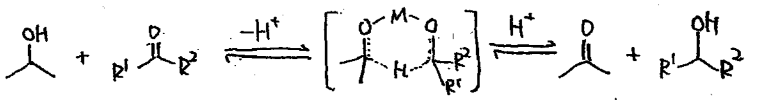
Basker Sundararaju, Mathieu Achard, Gangavaram V. M. Sharma, and Christian Bruneau*

J. Am. Chem. Soc. dx.doi.org/10.1021/ja203875d

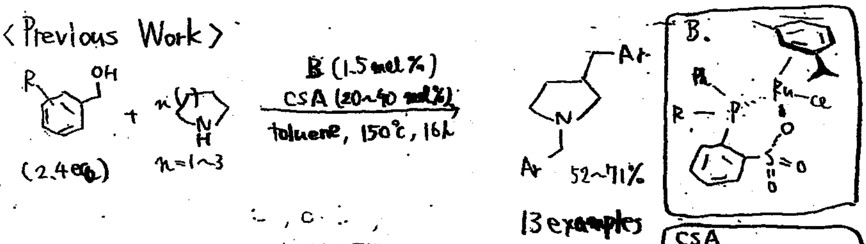
– Strategy



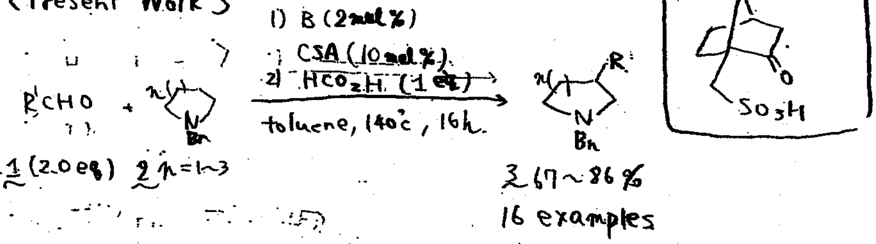
• Ru ··· Hydrogen transfer



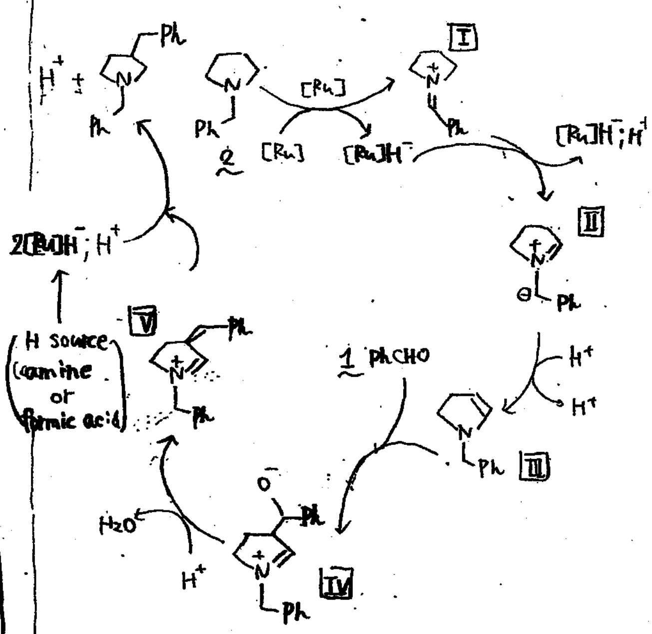
⟨Previous Work⟩



⟨Present Work⟩



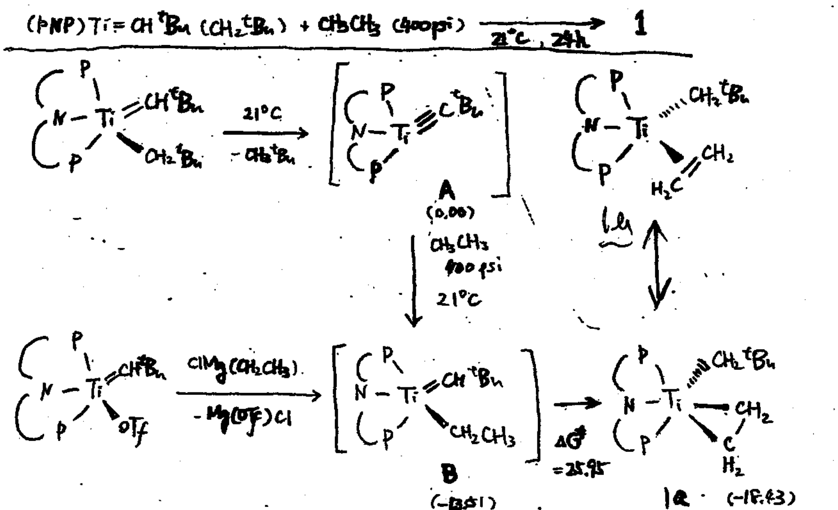
Reaction Mechanism



Room Temperature Dehydrogenation of Ethane to Ethylene

JACS 10.1021/ja20316m M1 矢野

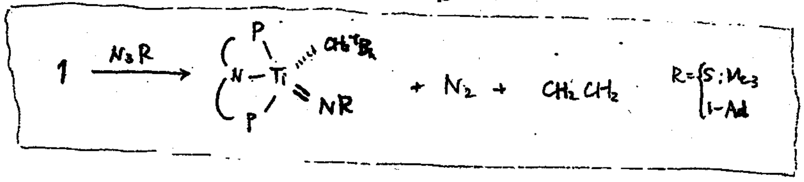
Vincent N. Cavaliere, Marco G. Crestani, Balaz Pinter, Maren Pink, Chun-Hsing Chen, Mu-Hyun Baik, and Daniel J. Mindiola



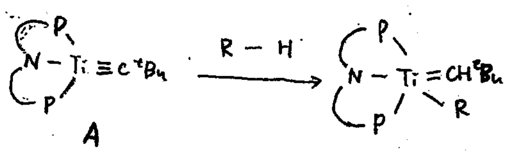
☆ 工業的なエタンのエチレンへの変換（クラッキング）の問題点、

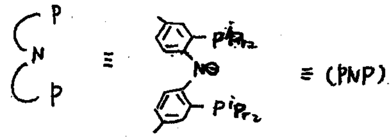
- 800℃以上の熱を必要とする
- CO_2が生成することによるロスがある

☆ Ir, Rh, Re の均一系脱水素触媒は高温を必要とするため、揮発性が高いアルカンにしか使えない



Previous Work





n-pentane →(A)→ 1-pentene

n-hexane →(A)→ 1-hexene

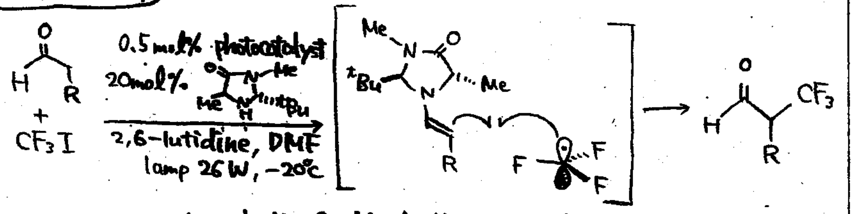
Photoredox Catalysis: A Mild, Operationally Simple Approach to the Synthesis of α-trifluoromethyl Carbonyl Compounds

B4 利根彩織

Phong V. Pham, David A. Nagib, and David W.C. MacMillan*

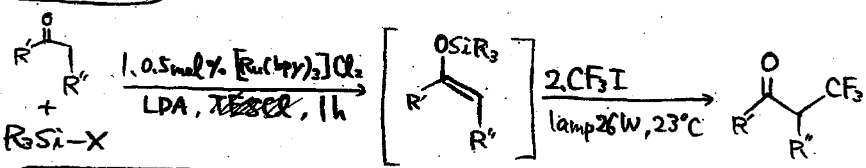
Angew. Chem. Int. Ed.
DOI: 10.1002/anie.201101861

Previous Work



David W. C. MacMillan, et. al, JACS, 2009, 131, 10875

This Work



Scheme 1. Proposed Mechanism

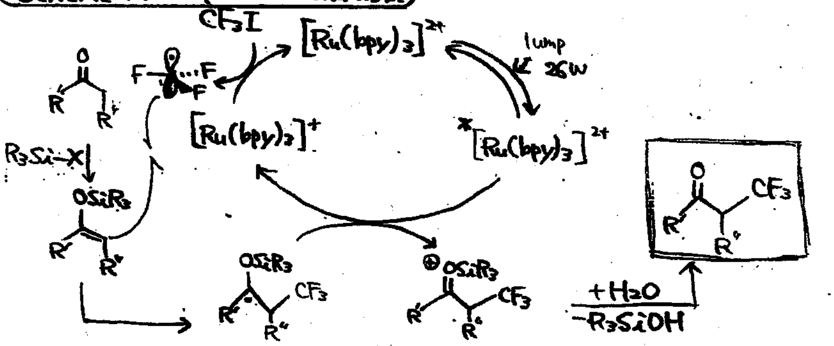


Table 1. Trifluoromethylation of enolsilanes

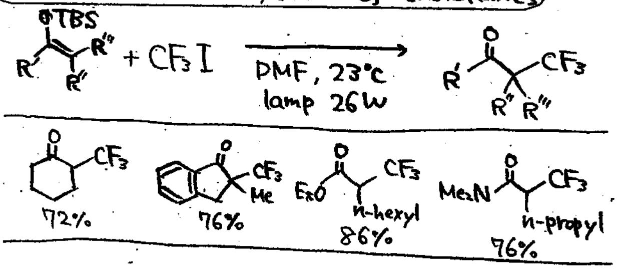


Table 2. Direct, one-pot α-perfluoroalkylation