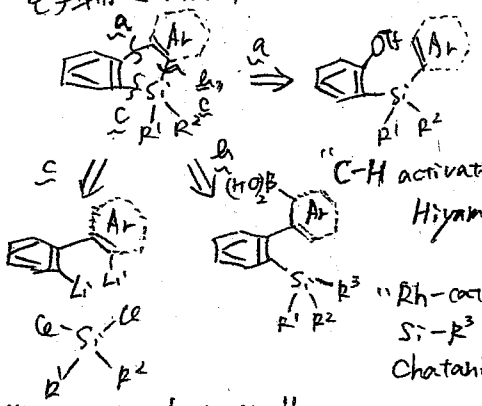
CT 1611 Youhei Takeda

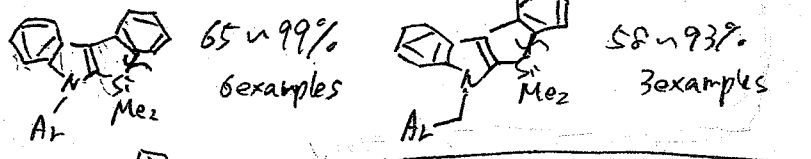
"Palladium-Catalyzed Synthesis of Benzosilolo[2,3-*b*]indoles via Cleavage of a C(sp^3)–Si Bond and Consequent Intramolecular C(sp^2)–Si Coupling"

Liang, Y.; Zhang, S.; Xi, Z.* *J. Am. Chem. Soc.* **2011**, *ASAP* (doi: 10.1021/ja.2024959)

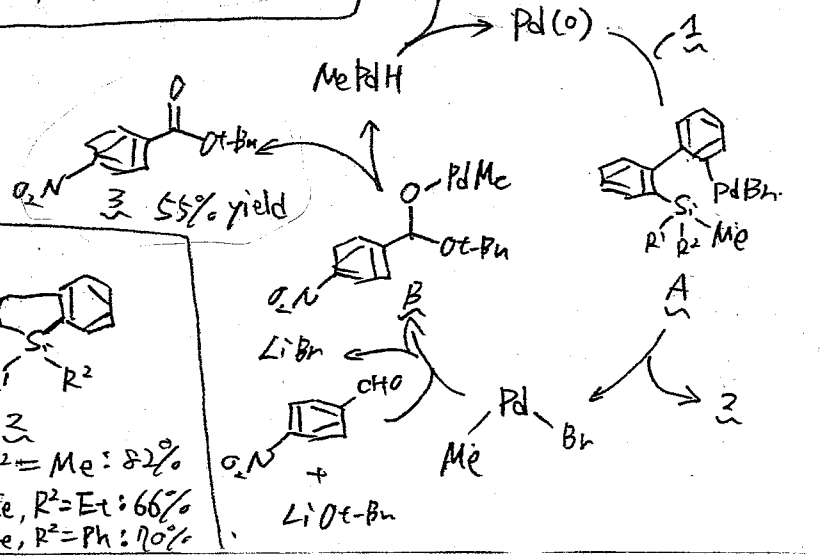
⊕ benzosilole は有機発光材料や電子輸送材料として使われている。



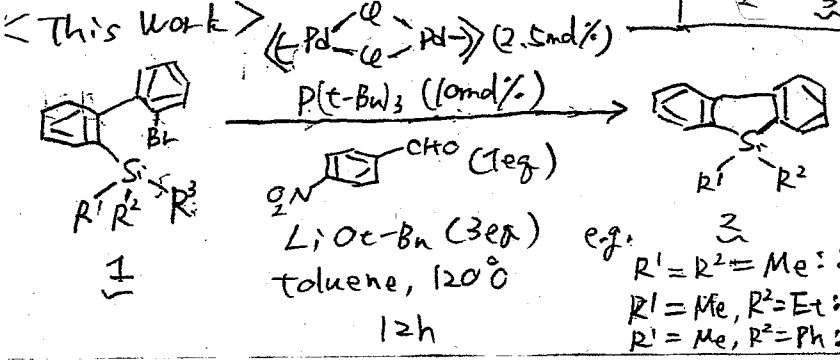
<Benzosilolo[2,3-*b*]indole synthesis>



<Mechanism>



<This Work>

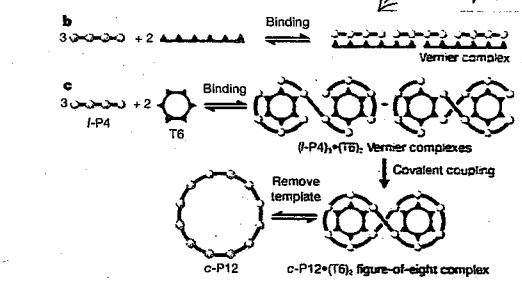


Vernier templating and synthesis of a 12-porphyrin nano-ring. 長町

Melanie C. O'Sullivan and Johannes K. Sprafke et al. *Nature*, 2011, 469, 72

This Work

テンプレート分子と 一体 最小化合数で複合体を形成!!

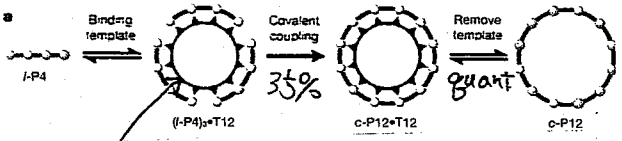


• バーニア法を用いてポルフィリンが12コ、共有結合でつながった ナノリングを合成。

直径4.7nm

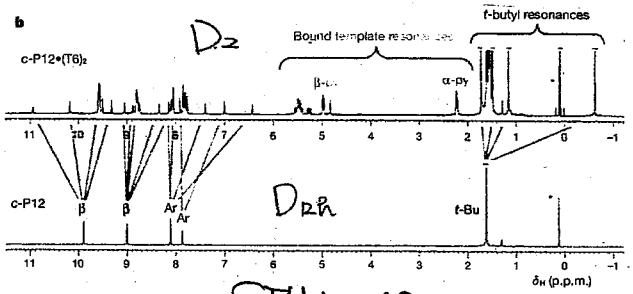
現在までに合成された π-共役ナノリングの中で最大。

• Vernier法を用いない場合。

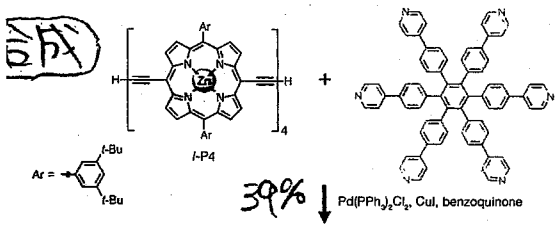


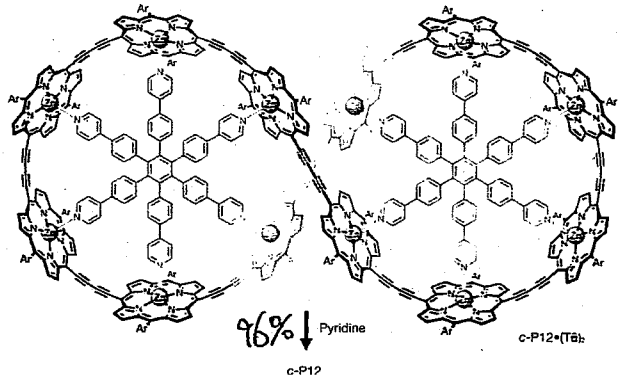
10 step以上の合成が必要!!

評価

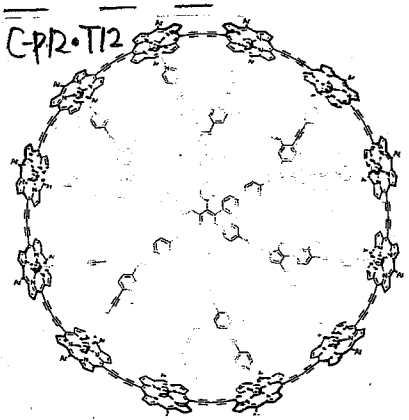


合成

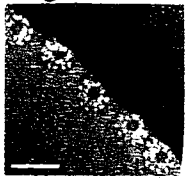




c-P12•T12



STM image



lp1 or lp2 + T6 ⇒ cP6 ができる。

結論 本法の確立により、リングの大きさが自在になる!!

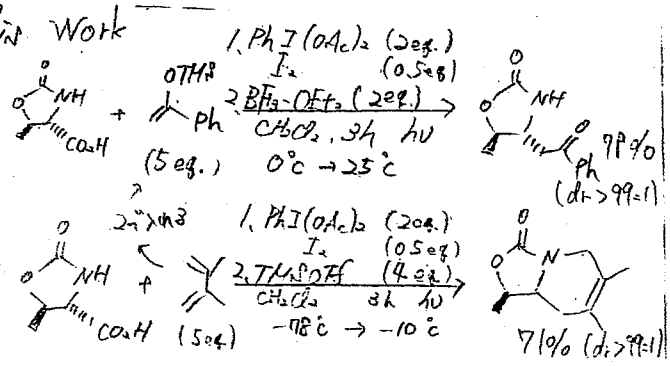
Sota Okumura

One–Pot Stereoselective Synthesis of 1,2–Amino Alcohol Derivative

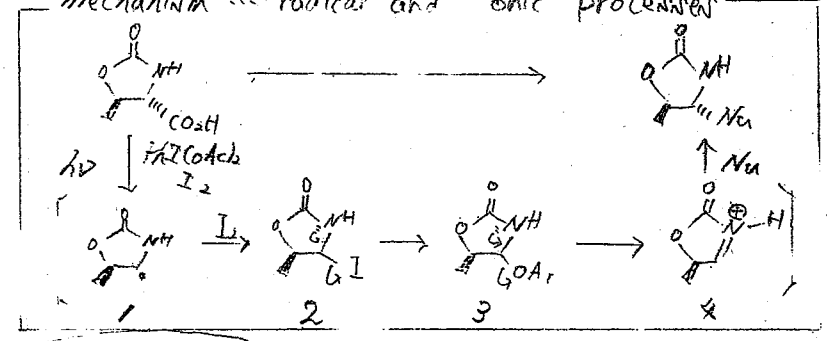
6/11

Alicia Boto* and Iván Romero-Estudillo *Org. Lett.* **DOI:** 10.1021/ol201173a

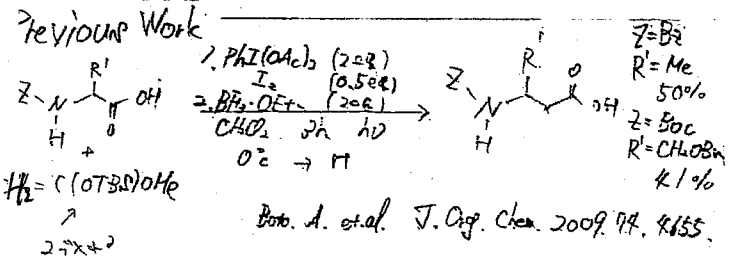
This Work



mechanism … radical and ionic processes

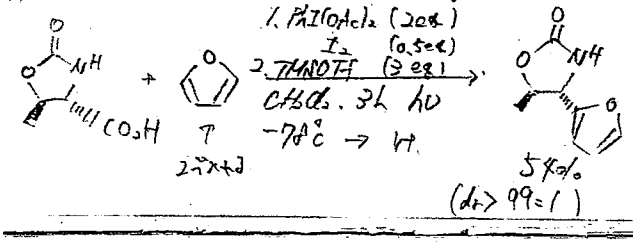


Previous Work

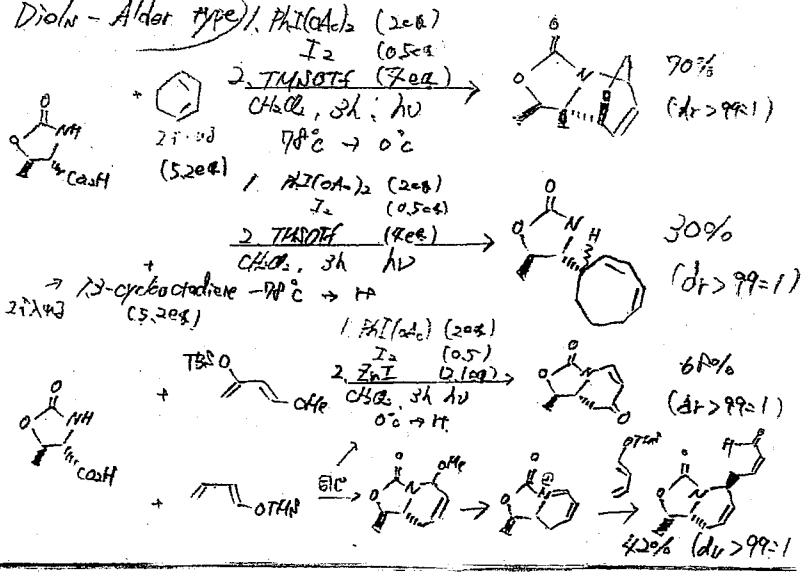


Boto. A. et.al. J. Org. Chem. 2009, 74, 4455.

Applied to electron-rich aromatic rings



Diels-Alder type



CT 2011/06/11

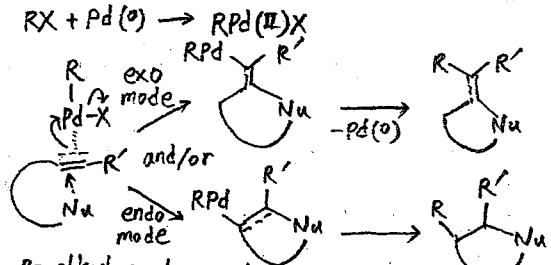
M2 Yuki Mitani

Synthesis of Alkylidenecyclopropanes by Palladium-Catalyzed Reaction of Propargyl-Substituted Malonate Esters with Aryl Halides by Anti-carbopalladation Pathway

Daishi Fujino,[†,‡] Hideki Yorimitsu,[*,‡] and Koichiro Oshima

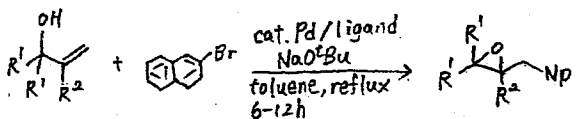
J. Am. Chem. Soc. (DOI: 10.1021/ja203062z)

Previous Work



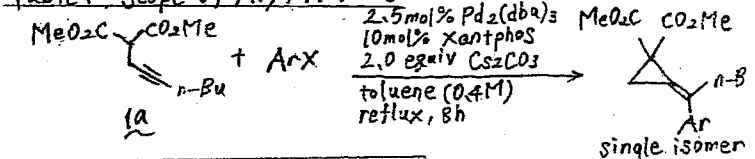
R = alkyl, aryl, vinyl, propargyl, allenyl, alkynyl
R' = aryl, alkyl
X = OAc, OTs, Cl, Br, I, OTf, OR''

Balme, G. et al. Synthesis 2013, 14, 2115.



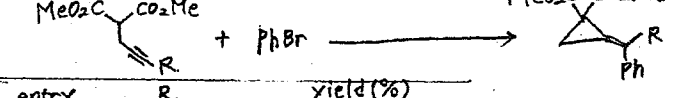
Oshima, K. J. Am. Chem. Soc, 2009, 131, 2052.

Table 1. Scope of Aryl Halides



entry	ArX	yield (%)
1	PhOTf	97
2	1-naphthyl-Br	91
3	4-$CF_3C_6H_4$Br	90
4	4-NCC_6H_4Br	92
5	2-MeOC_6H_4Br	60

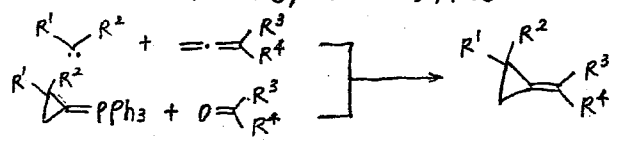
Table 2. Scope of Propargyl Malonate Esters



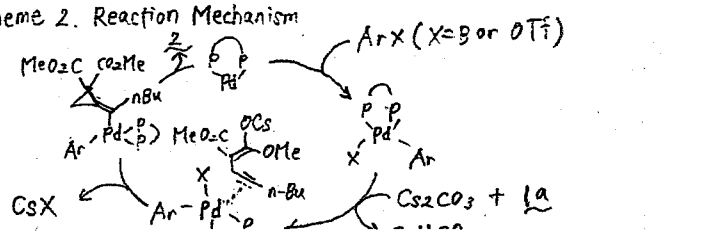
entry	R	yield (%)
1	Me	73
2	t-Bu	0
3	Ph	70
4	4-$CF_3C_6H_4$	53

This Work

Scheme 1. Conventional Synthesis of ACPs



Scheme 2. Reaction Mechanism



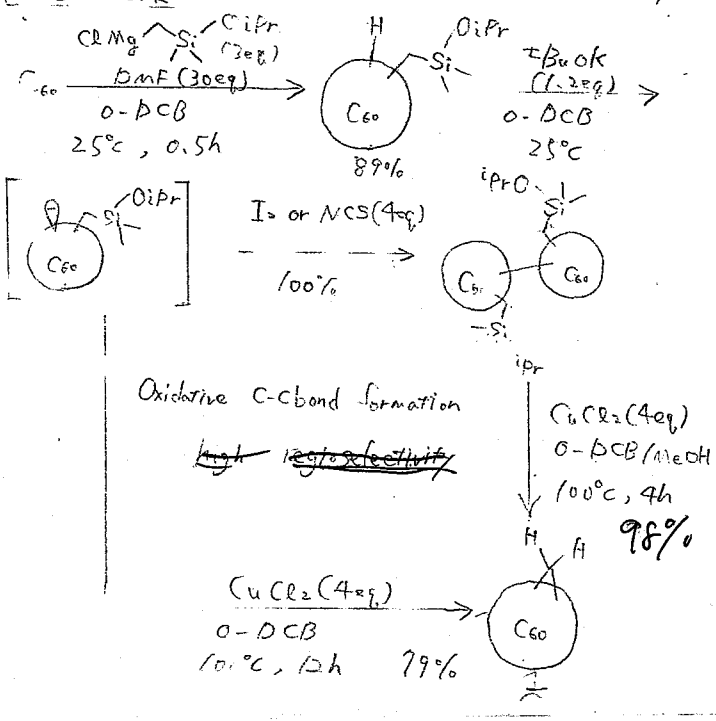
A Scalable Synthesis of Methano[60]fullerene and Congeners by the Oxidation Cyclopropanation Reaction of Silylmethylfullerene

Y. Matsuo, E. Nakamura, *et al. J. Am. Chem. Soc.* **2011**, *133*, 8086 **Hajime Kawai**

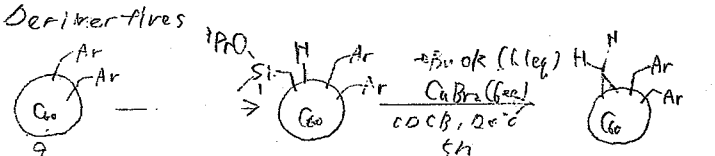
☆ Cyclopropanation

- 1,3-dipolar cycloaddition of diazomethane CH_2N_2
- The use of diiodomethane CH_2I_2 } low yield

This work



Synthesis of the 58π-Electron Methanofullerene Derivertives



- regioselective cyclopropanation

Ar	C_{60}	1	9a	11a	11b	14
LUMO level(eV)	−3.90	−3.59	−3.60	−3.47	−3.47	−3.51

LUMO Levels for Fullerene Derivertives

p-n heterojunction: n-type / p-type — Active layer → bulk heterojunction (BHJ): n-type + p-type

	fullerene	PCE (%)
p-n	9a	1.0
	11a	1.9
BHJ	9a	1.6
	11a	3.4

Introduction of the methylene group raise { LUMO level, Voc, PCE

• テトラベンダジオール ⊙ Voc: PCBM より高い。

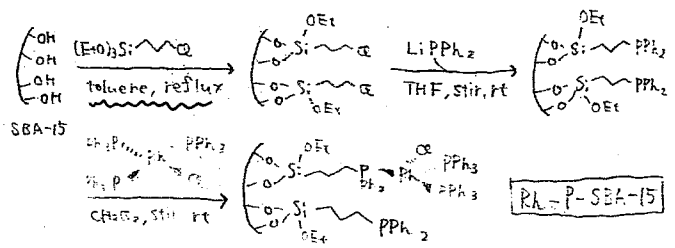
tighly regio- and stereoselective hydrothiolation of acetylenes with thiols catalyzed by a well-defined supported Rh complex

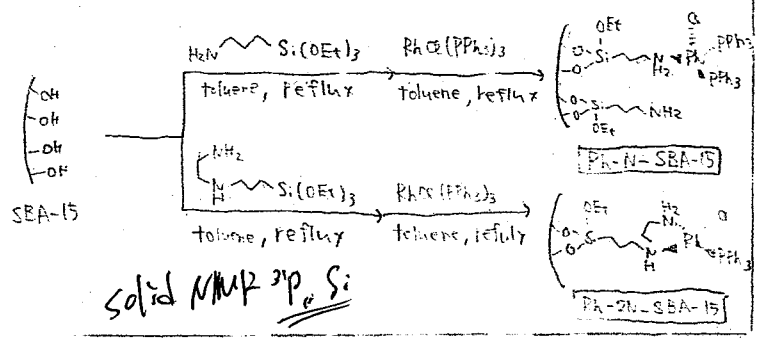
Yong Yang and Robert M. Rioux

M1 鈴木研究室
Chem. Commun.
DOI: 10.1039/c1cc11605c

金属触媒を担持したシリカ → 回収・再利用が可能

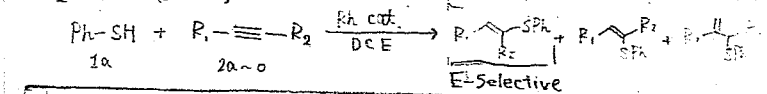
• Rh触媒を担持したSBA-15の合成





Solid NMR ^{31}P, ^{29}Si

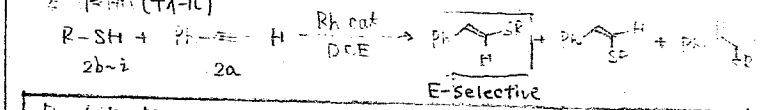
• 基質展開 (アルキン)



R_2=H のとき R_1 = Ph, 4-Me-Ph, 2-Me-Ph, 3-Me-Ph, 4-MeO-Ph, 2-MeO-Ph, 4-F-Ph, 4-Br-Ph, n-C_5H_{11}, n-$C_{10}H_{21}$, HO-(C_2H_4), cyclohexene

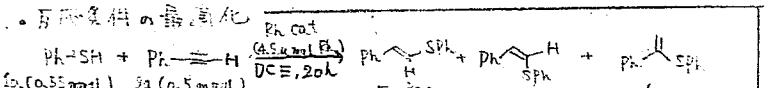
R_2=Me のとき R_1 = Ph ※ R_2=Ph, R_1=Ph のとき no reaction

• 基質展開 (チオール)

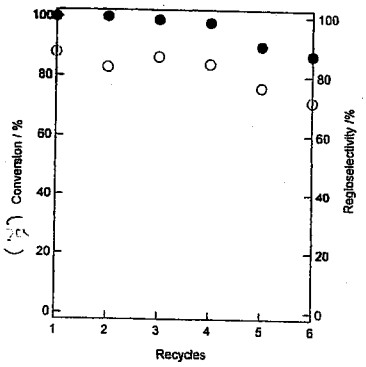


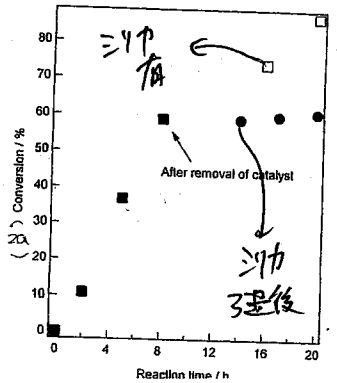
R = 4-Me-Ph, 4-MeO-Ph, 4-Cl-Ph, 4-Br-Ph, Ph-CH_2, cyclohexyl, CH_3CH_2, CF_3CH_2

• 反応条件の最適化



Entry	Catalyst	Conv/%	(3+E):4aa	E:Z (3aa)
1 (45 min)	$RhCl(PPh_3)_3$	98	94 : 6	100 : 0
2	Rh-N-SBA-15	94	>99 : 1	99 : 71
3	Rh-2N-SBA-15	95	>99 : 1	1 : 99
4	Rh-P-SBA-15	88	>99 : 1	100 : 0





Divergent Regioselectivity in the Synthesis of Trisubstituted Allylic Alcohols by Nickel- and Ruthenium-Catalyzed Alkyne Hydrohydroxymethylation with Formaldehyde

M1 矢野 和樹

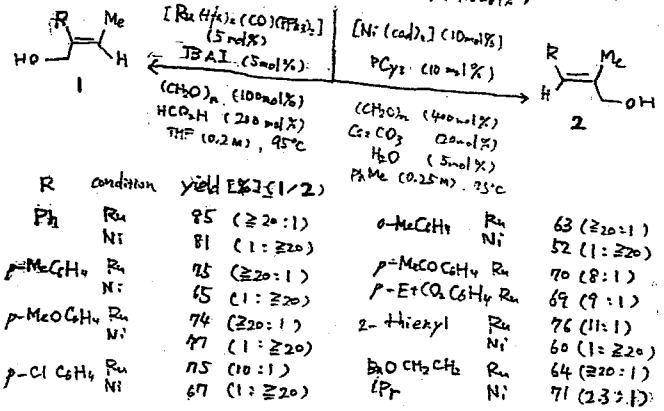
Cory C. Bausch, Ryan L. Patman, Bernhard Breit, and Michael J. Krische

Angew. Chem. Int. Ed. **2011**, *50*, 5687.
DOI: 10.1002/anie.201101496

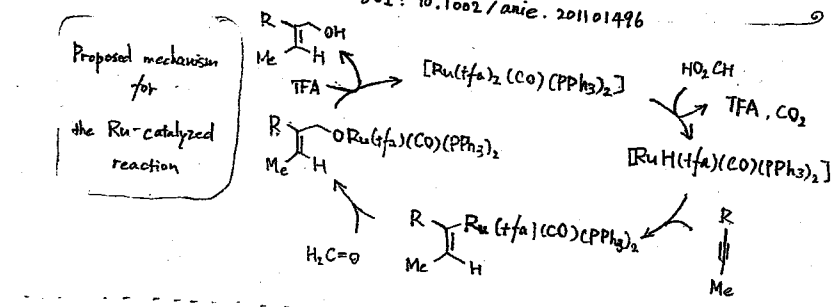
位置, 立体選択的なアリルアルコールの合成

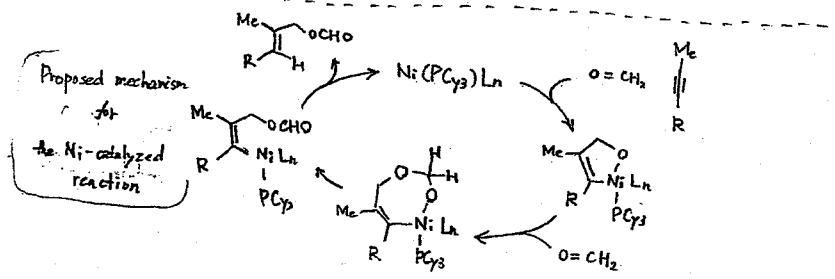
1. 化学量論量の有機金属試薬を必要とするプロセス
   - プロパルギルアルコールからビニルヨージドへの変換に続いて, $LiCuR_2$ を使用し合成するプロセス
   - アルキンと Grignard 試薬の反応による合成
2. 量論還元剤 (Et_3B, Et_2Zn, $HSiR_3$) を必要とする
   Ni 触媒 アルキン-カルボニル還元的カップリング

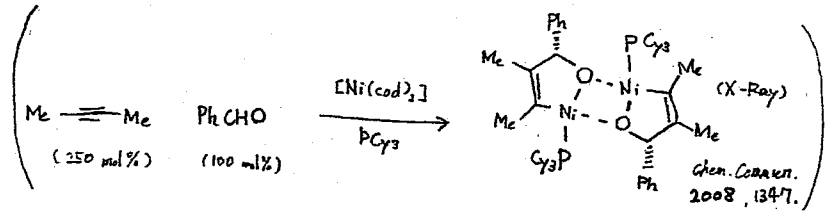
This Work 量論還元剤を必要としない Ni 触媒ヒドロヒドロキシメチル化



R	condition	yield [%] (1/2)			
Ph	Ru	85 (≧20:1)	o-MeC6H4	Ru	63 (≧20:1)
	Ni	81 (1:≧20)		Ni	52 (1:≧20)
p-MeC6H4	Ru	75 (≧20:1)	p-MeCOC6H4	Ru	70 (8:1)
	Ni	65 (1:≧20)	p-EtCO2C6H4	Ru	69 (9:1)
p-MeOC6H4	Ru	74 (≧20:1)	2-thienyl	Ru	76 (11:1)
	Ni	47 (1:≧20)		Ni	60 (1:≧20)
p-ClC6H4	Ru	75 (10:1)	BnOCH2CH2	Ru	64 (≧20:1)
	Ni	67 (1:≧20)	iPr	Ni	71 (2.3:1)





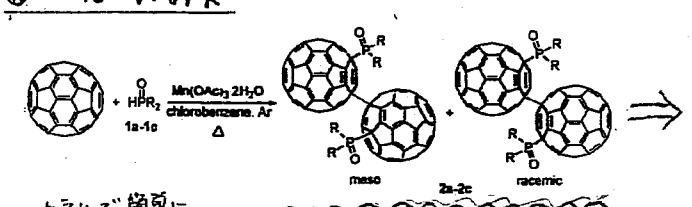


Manganese(III) acetate-mediated radical reaction of [60]fullerene with phosphonate esters affording unprecedented separable singly-bonded 60]fullerene dimers†

Guan-Wu Wang,*[a] Cong-Zhou Wang,[a] San-E Zhu[a] and Yasujiro Murata*[b] **DOI: 10.1039/c1cc10820d**

CT: 2011/6/11
B4 榎島 悟
(Chem. Commun.)

This Work



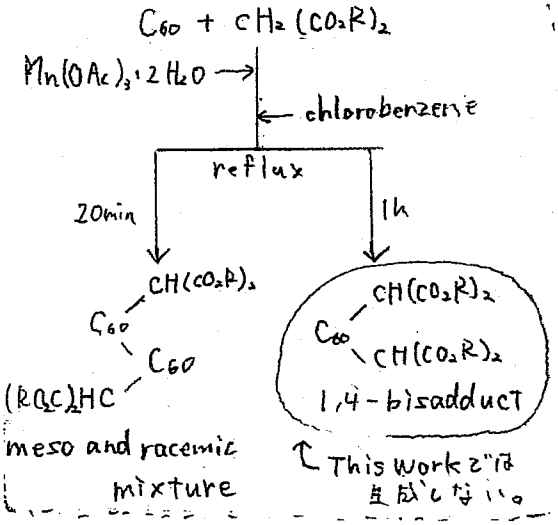
カラムで簡単に分けれる。(シリカゲル)

初めて2つの isomer を単離することに成功した。

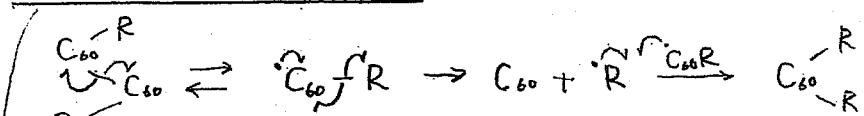
Substrate 1	Molar ratio of C_{60}/1/$Mn(III)$	T(℃)	t(min)	yield (%)
$HP(O)(OMe)_2$ … 1a	1:2:2	135	50	29 (88)
$HP(O)(OEt)_2$ … 1b	1:2:2	135	50	28 (88)
$O=P(-H)(-O-)_2$ … 1c	1:2:4	100	90	34 (97)

↑ それぞれ対応する fullerene dimer を与えた。(2a-2c)

Previous Work



- 1,4-bisadduct 生成の機構 (提唱されているもの)



(・$•P(O)R_2$ と $•C_{60}P(O)R_2$ が極度に結合をつくりにくい?
・$•C_{60}P(O)R_2$ から $•P(O)R_2$ の生成が非常に早い?)

- トルエン溶媒での反応

・$PhCH_2C_{60}P(O)R_2$ は全く生成しない (皮膚では反応例あり)
↓
クロロベンゼン溶媒と同じ生成物 yield: 15% (83%)

•C と •P とはフラーレン系での挙動が違う。
(NとPの違いも報告されている)

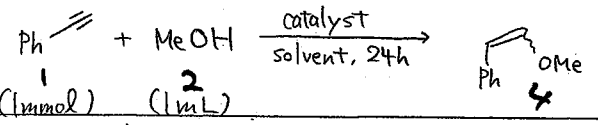
Rhodium – Catalyzed Anti-Markovnikov Intermolecular Hydroalkoxylation of Terminal Acetylenes

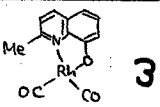
Masataka Kondo, Takuya Kochi, and Fumitoshi Kakiuchi*

JACS 133, 32-34
DOI : 10.1021/ja1097385

B4 利根紗織

Table 1. anti-Markovnikov Addition of 2a to 1a



entry	catalyst	temp	solvent	yield [%]
1	5mol%  **3**	65°C	—	22%
	• hydroformyl 化			
2	5mol% $[RhCl(CO)_2]_2$	65°C	—	< 5%
3	5mol% $[RuCl(CO)_3]_2$	65°C	—	not detected
4	5mol% $IrCl(CO)(PPh_3)_2$	65°C	—	not detected
5	5mol% **3**	65°C	toluene	32%
6	5mol% **3**	65°C	THF	29%
7	5mol% **3**	65°C	DMF	44%
8	5mol% **3**	65°C	DMA	59%
9	5mol% **3**	65°C	Et_3N	7%
10	5mol% **3**	65°C	pyridine	not detected
11	5mol% **3**	70°C	DMA	62%
12	2mol% **3**	70°C	DMA	80%

Scheme 1. Effect of Ligands for Hydromethoxylation of 1a

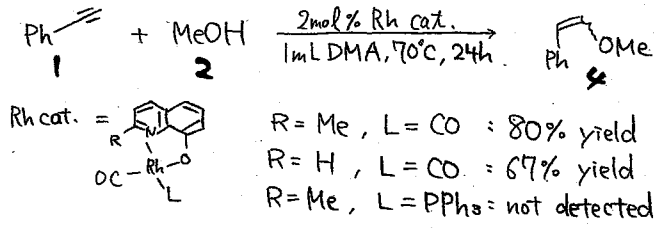
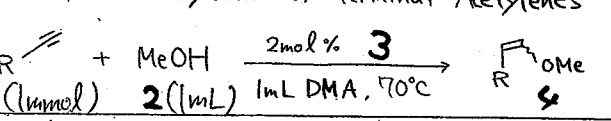
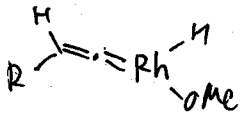


Table 2. Hydromethoxylation of Terminal Acetylenes



entry	1	R	time	yield	Z : E
1	1a	p-$CF_3C_6H_4$	48h	92%	94 : 6
2	1b	p-NCC_6H_4	48h	85%	95 : 5
3	1c	p-$MeO_2CC_6H_4$	48h	82%	94 : 6
4	1d	p-MeC_6H_4	6days	64%	88 : 12
5	1e	p-$MeOC_6H_4$	7days	64%	87 : 13
6	1f	2-naphthyl	48h	55%	91 : 9
7	1g	1-cyclohexenyl	3days	27%	50 : 50
8	1h	Ph_3C	48h	69%	100 : 0

このように、末端アルキンへ アルコールが anti-Markovnikov 付加した生成物が得られたが、その反応機構についてはまだわかっていない。



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