040421 D3 N. Kumagai

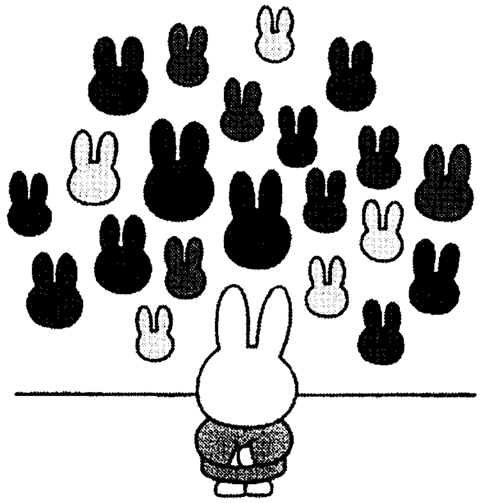
imaginary

TACTICS FOR TARGET ORIENTED SYNTHESIS

—thought experiment—

target

target



mass production

mass production

template

template

I. de novo Creation

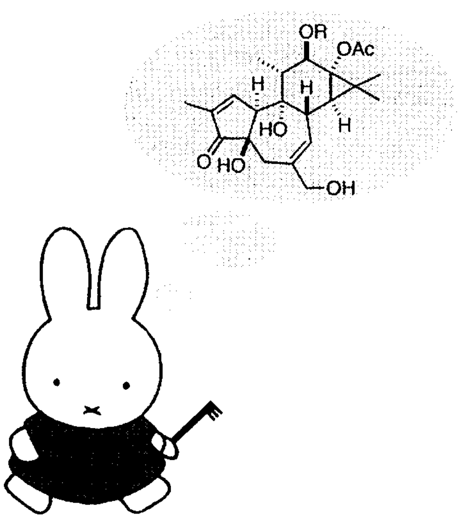
*Atomic manipulation

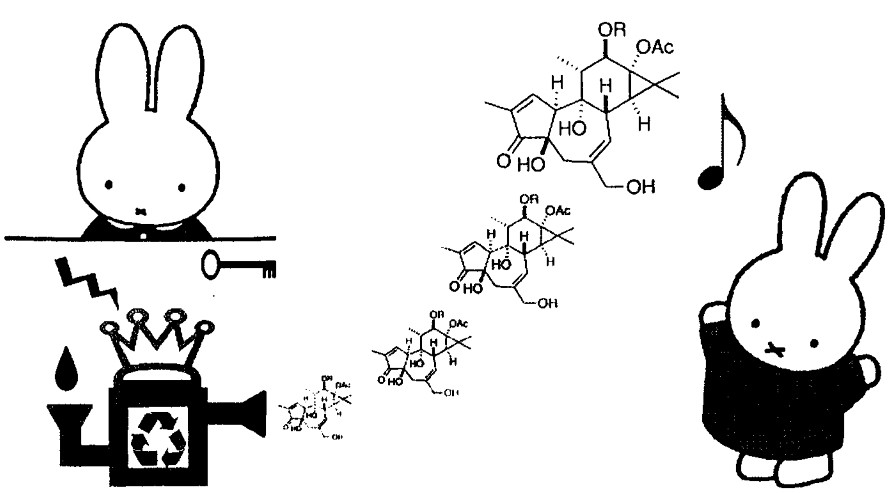
*Laser lithography

II. Aquired expertise

*Exploiting biochemical process

*Steady state sequence





年輩だが著名な科学者が何かができると言えば、それはほぼ間違いなく正しいが、
その人が何かができないと言えば、それは間違っている公算が非常に高い。
——アーサー・C・クラーク

I. *de novo Creation*

Summary: Atomic Gas Laser Lithography

A concept, ATOM

- atheism
- rare example:
  toward the understanding
  of the Universe.

Reukippos
Democritus
[~B.C.500]

ÁTOMOS
a + témnein + os

Alistotle
[B.C.384-322]

OBJECTION
1. How can atom keep moving?
2. Nothing is nothing.

Element

Fire — warm — Air
dry — 4-element theory — wet
Soil — cold — Water

Intuitive
meet the common sence

alchemy

最も生き生きとした想像力が生みだす思想のうちで，賢者の石という考えほど，人間の精神や能力にいつも力強くはたらきかけたものはない．この考えがなければ，化学は今日のように完成したものとはならなかったであろう……．(というのも)，賢者の石が現実には存在しないということを知るためには，……入手しうるあらゆる物質を観察し，検討することが絶対に必要だったからである．

J. von Liebig [1803-1873]

Physics

Galilei
[1564-1642]
~~Vacuum~~

O. von Guericke
[1602-1686]
~~alistotle~~

R. Hooke
[1635-1703]

corpuscular philosophy

I. Newtow
[1642-1727]
- acceptance of atom
- no progress

X

Chemistry

R. Boyle
[1627-1691]

Skeptism
Experimental

木の枝についていえば，火でこれを分解して得られるのは，元素ではなく，複合物であり，火は木を別の形状のものへとかえただけなのである．炎は燃えている物体のなかにある硫黄部分にすぎないように思われる．熱せられて最終的に得られる水は元素の水というには程遠く，かなり塩を含んでいるし，凝固物の性質を示す．それゆえ，内科医は，単純な水ではまったく効果がないのに，数種の植物を沸騰させて得た樹液が病気にきくと判断しているのである．煙も，元素の空気とするには程遠い．それを蒸留すると，油を生じるし，この油も土を含んでいるので，煙はそれ自体まだ複合物である．煙は塩に富み，土を肥沃にしやすく，痛みを与え，目を潤ませるように思われる（普通の水の煙では，そうしたことは起こらない）．そして疑問の余地がないことだが，煙から簡単に抽出できた純粋な塩を用いて，私は最近，白色で揮発性に富む浸透剤を得た．

自然界の構成についていえば，元素があらかじめ存在していたと想定するように，自然界には何らかの初源的で単純な物体があり，これらから一切の事物がつくられているのだと考えねばならない理由があるとは思えない．むしろ，こう考えてはどうだろうか．よくいわれるように，自然は質料を何らかの単純で均質な実体へと分解せずとも，物体の微小部分をさまざまに組みかえることにより，さまざまな物体を生みだしているのである．

物体を分析してみて，少なからず不思議に思ったのは，いや，驚かされたのは，外見からはまったくそうはみえないのに，いくつかの物体はかなりの量の水から構成されていることである．いくつかの固く頑丈な木からは，他のどの元素にもまして水だけが多く得られる．ウナギを蒸留すると，残りかすの他に，いくらかの油，精気，揮発性の塩が得られるが，生じた水はこれら以上にはるかに多く，……水以外の生成物全部を合わせても，凝固した粘液程度しか得られないくらいなのである．

J.-B. van Helmont
[1577-1644]
Quantitative Experiments

すべての植物が直接的に，また実質的に元素の水だけに由来するということを，私は次のような実験から知った．かまどで乾燥させた土200ポンドを土製容器にいれ，雨水をかけた．そこに重量5ポンドの柳の木を植えた．5年後にこの木は重量169ポンド3オンスほどに成長した．この間，雨水（または蒸留水）以外のものは何も与えなかった．この大きな容器を地面におき，表面が錫でできている，小穴のたくさんあいた鉄のふたでおおった．4年間，秋に落葉する葉については重量を調べなかった．最終的に，容器の土をもう1度乾燥させたところ，上記の200ポンドの土は2オンスほど減少していることがわかった．したがって，総重量164ポンドになるこの柳の木の本体，樹皮，根は水だけから生じたのである．

2 element
- water
- ferment

物体の始源であり，また形成の要因である物質は，二つだけしかない．つまり，物体を構成している元素の水と発酵素である．

G. Stahl
[1660-1734]
- combustion
- phlogiston theory

Metal (metal source + phlogiston)	⟶	Metal ash + phlogiston (metal source)
	coal (phlogiston)	

理性的な人は世界に自分を合わせる。理性的でない人はあくまでも世界を自分に合わせようとする。したがって、すべての進歩は理性的でない人にかかっている。
——ジョージ・バーナード・ショー(49)

Physics ········ phlogiston theory ········ **Chemistry**

H. Cavendish [1731–1810]
"inflammable gas" H_2
(metal + H_2SO_4)

G. Black [1728–1799]
"fixed gas" CO_2

G. Priestley [1733–1804]
~20 kinds of gas...

~~**Air = an element**~~

A. L. Lavoisier [1743–1794]

L.-B. Guyton [1737–1816]
combustion of metal
↓
weight gain → phlogiston?

~~**Metal** [metal source + phlogiston] → **Metal ash** + **phlogiston**~~
~~(metal source)   coal (phlogiston)~~ [1]

Metal + **Air** [air source + **phlogiston**] → **Metal ash** [metal + air source] + **light, heat** [**phlogiston**] [2]
gas

Black's "fixed air" (CO_2) ⇨ Metal + $\mathbf{CO_2}$?? → Metal ash + light, heat

! **HgO → Hg + combustible gas (O_2)**

oxygen based combustion theory

[3] **Metal + O_2 → Metal ash + *Caloric*** [•universal •origin of expansion •quantitive] ↔ phlogiston

....only phlogiston explained the following...

Metal [metal source + phlogiston] + **acid** → **Metal salt** [metal source] + **inflammable gas (H_2)** [phlogiston] [4]

Metal ash [metal source] + **acid** → **Metal salt** [metal source] + **No gas emmition** [5]

inflammable gas [H_2] + air → H_2O [6]

Cavendish's view

H_2 [H_2O + phlogiston] + O_2 [H_2O - phlogiston] → H_2O [7]

Lavoisier's view

H_2O is not an element

~~phlogiston~~

Metal + acid [contains H_2O] **→ Metal oxide + inflammable gas (H_2)** [8]

Physics

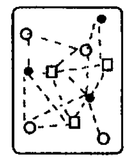
以上の考察はすべて，私が提起し，(1773年に)証明し，何度も繰り返し述べてきたことを確証している．これまでの化学者たちは，フロギストンを曖昧な原質にしてしまった．この原質は厳密に定義されておらず，そのため，説明のために必要とされる性質なら何でももっているような物質になってしまった．あるときには軽い物質であり，別の場合には重量がない物質とされ，また，遊離した火であると同時に，土と結合した火でもあり，容器の小孔を透過できるかと思えば，できないといわれる．苛性の説明に使われる一方で，苛性ではないことの説明にももちだされるし，透明かつ不透明で，有色とも無色ともいわれる．フロギストンは，休む間もなく形をかえる変幻自在のプロテウスである．

Chemistry

ラヴォアジエは1794年5月8日にギロチンにかけられた．数学者ラグランジュは，「彼の首を切るには一瞬で済むが，同じ頭を生みだすにはおそらく100年でも足りないだろう」と述べた．その100年を経た1890年代に，ラヴォアジエを記念する公共の像が建立された．ところが数年後，彫刻家が模写した顔は，ラヴォアジエ最後の数年間に科学アカデミーの事務局長を務めていた哲学者コンドルセのものであることが判明した．資金不足のため修正は行われず，結局，実際的なフランス人は，いずれにせよ鬘をつけた人物は皆同じにみえるなどといって済ませてしまった．この像は第二次世界大戦中に鋳潰されてしまい，再建されていない．ラヴォアジエの真の記念碑は化学それ自体なのである．

1. Air plays critical role in some chemical reactions.
2. Air is not an element.
3. The cocept of **gases**—matter with caloric.
4. Component of matter, **element**.

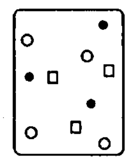
Boyle, Newton:
corpuscular philosophy
(粒子論)



conventional view

J. Dalton
[1766–1844]

- meteorological observation.
- No bonds between gases.



Daiton's view

repulsive particle

repulsive gas atom
due to **caloric**

A + B ⟶ AB ~~(A_nB_n)~~

B. Thompson
[1753–1814]
caloric??

relative atomic weight

J. J. Berzelius
[1779–1848]

- analyzed >2000 material.
- accurate data.
- **electrochemical dualism.**

A. Volta
[1774–1827]
Voltic pile

mechanical view of Temp. & Pressure

Royal Society

H. Davy
[1778–1829]
electrolysis:
isolation of Na
(Lavoisier's prediction)

1820 X
J. Herapus
X
J. J. Waterston
1845

atomic view was rejected

nearly same...

R. J. Clausius
[1822–1888]
1857
mechanical view of Temp. & Pressure

average velocity of particles

A. Laurent
[1808–1853]
arrangement of elements

J. C. Maxwell
[1839–1879]
statistical treatment

J. W. Gibbs
[1839–1903]
thermodynamical view
without the concept, atom

A. Williamson
[1824–1904]

H, H] O	R, H] O	R, R] O
water	alcohol	ether

- water type
- dynamic view of reaction

L. Boltzmann
[1844–1906]

- detailed expression of thermodynamical view with statistical treatment.
- severe situation

M. Planck
[1858–1947]
black body radiation spectra

A. Einstein
[1879–1955]
representation of Brownian motion with atomic mechanics.

F. A. Kekulé
[1829–1896]
valency of carbon

「不測のものを予測しない者はその存在に気づかず、永遠に発見できず、近づいていくことすらできないだろう。」
〈ヘラクレイトス〉

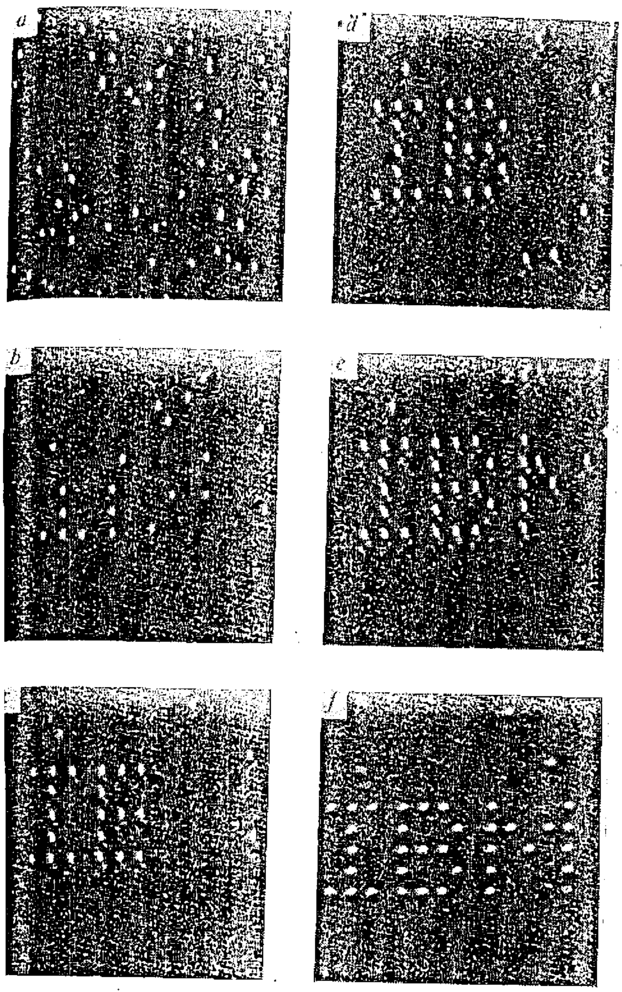
Atomic manipulation … first impressive example.

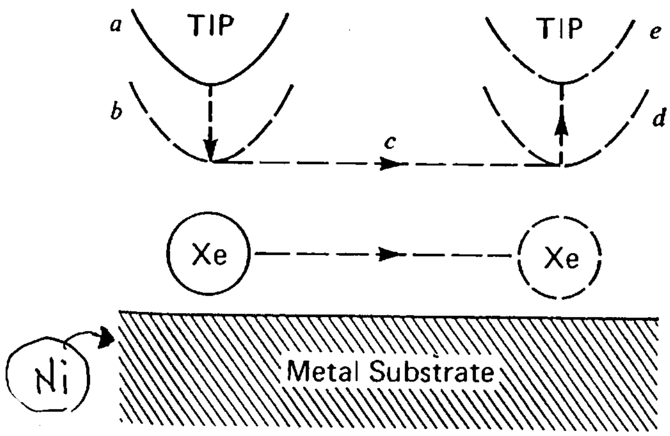
Positioning single atoms with a scanning tunnelling microscope

走査トンネル顕微鏡 Nature, 1990, 344, 524.

D. M. Eigler & E. K. Schweizer*

IBM Research Division, Almaden Research Center, 650 Harry Rd, San Jose, California 95120, USA

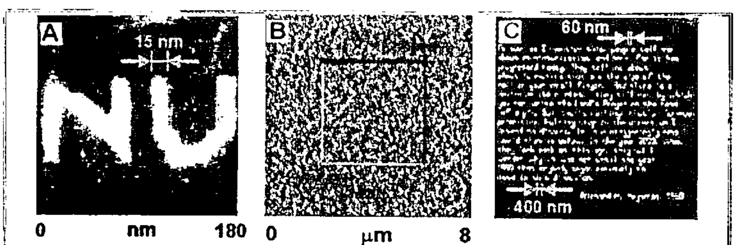




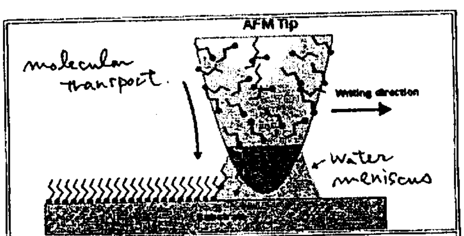
A schematic illustration of the process for sliding an atom across a
. The atom is located and the tip is placed directly over it (*a*). The
wered to position (*b*), where the atom–tip attractive force is sufficient
 the atom located beneath the tip when the tip is subsequently
across the surface (*c*) to the desired destination (*d*). Finally, the tip
rawn to a position (*e*) where the atom–tip interaction is negligible,
the atom bound to the surface at a new location.

DPN: Dip-pen Nanolithography:

$HOOC(CH_2)_{13}SH$ on Au surface



A) Ultra-high resolution pattern of mercaptohexadecanoic acid on atomically-flat gold surface. B) DPN generated multi-component nanostructure with two aligned alkanethiol patterns. C) Richard Feynmann's historic speech written using the DPN nanoplotter.



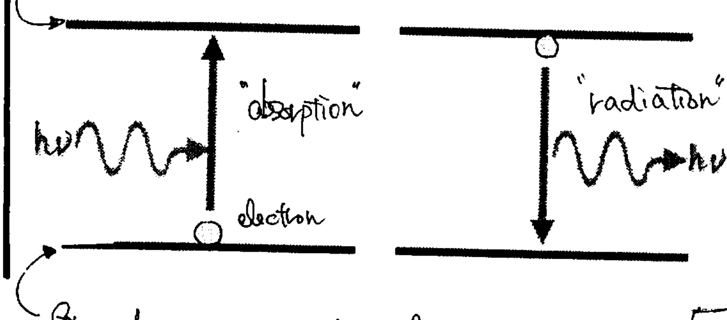
Dip-Pen Nanolithography: Transport of molecules to the surface via water meniscus.

2- dimensional manipulation ⟶ 3- dimensional manipulation.

⇑ LASER COOLING

- LASER : Light Amplification by Stimulated Emission of Radiation.

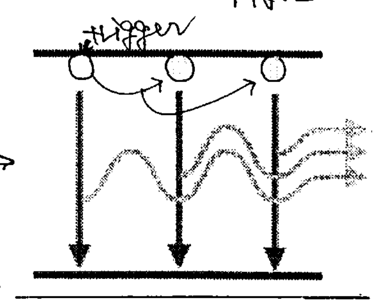
Fig. 1



Normal Radiation

LASER ... ⟶

Fig. 2



Stimulated Emission of Radiation

⇓ simultaneous.

⇓ coherent

Fig. 3.

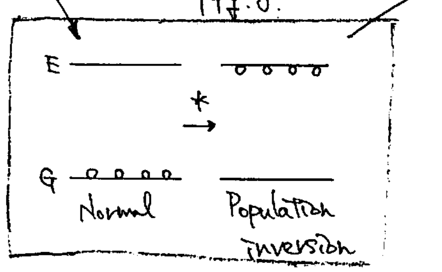
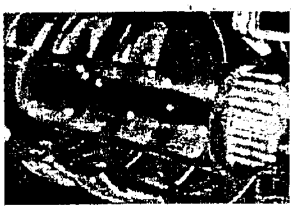
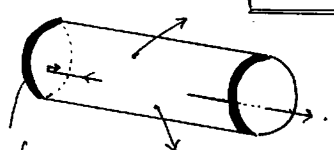


Fig. 4.





through with Intensity > I.

100% reflection

Light Amplification

LASER COOLING Ultra accute cooling of atoms or ions.

∼ mK, μK, nK temp.

The Nobel Prize in Physics 1997

"for development of methods to cool and trap atoms with laser light"

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

English
French
German
Swedish

Press Release: The 2001 Nobel Prize in Physics

New State of Matter Revealed: Bose-Einstein Condensate

To cool atom = To make Δv narrow.

$$\Delta v = \sqrt{\frac{k_B T}{M}}$$, at RT, 100 ∼ 1000 m/s.

(Δv:) velocity distribution.

(k_B : Boltzmann const.
M : atomic mass.
h : Planck const.)

thermal de Brógile wavelength

$$\lambda_{th} = \frac{h}{\sqrt{2\pi M k_B T}}$$

Ex) ^{87}Rb
300K : λ = 10 pm
200nK : λ = 0.4 μm

Cold atoms and quantum control

Steven Chu

Physics Department, Stanford University, Stanford, California 94305-4060, USA

are inevitable. Not surprisingly, these new research opportunities have stimulated many researchers to think about how to exercise further quantum control over still larger ensembles of atoms and photons, and how to exploit these systems in new ways. To quote Yogi Berra, the noted American philosopher and former catcher for the New York Yankees, "it is difficult to make predictions, especially about the future". Nevertheless, I predict that the most exciting developments are yet to come. □

Nature 2002, 416, 206.

○ A Brief Principle of Laser Cooling.

Fig. 1

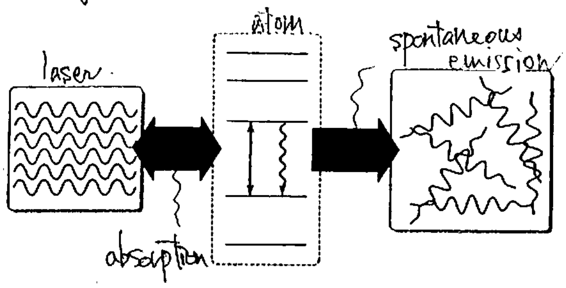


Fig. 2.

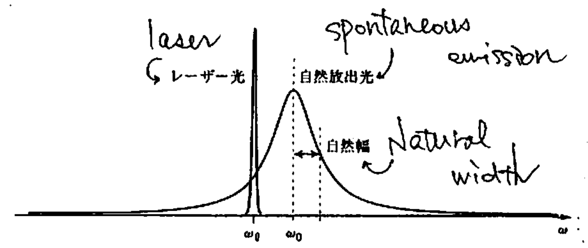
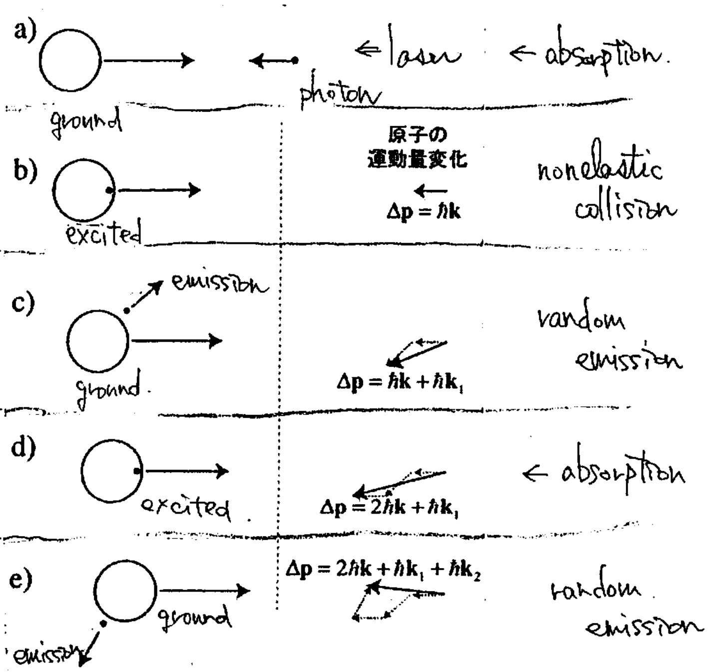


図 1.2 原子を冷却するためのレーザー光の周波数.

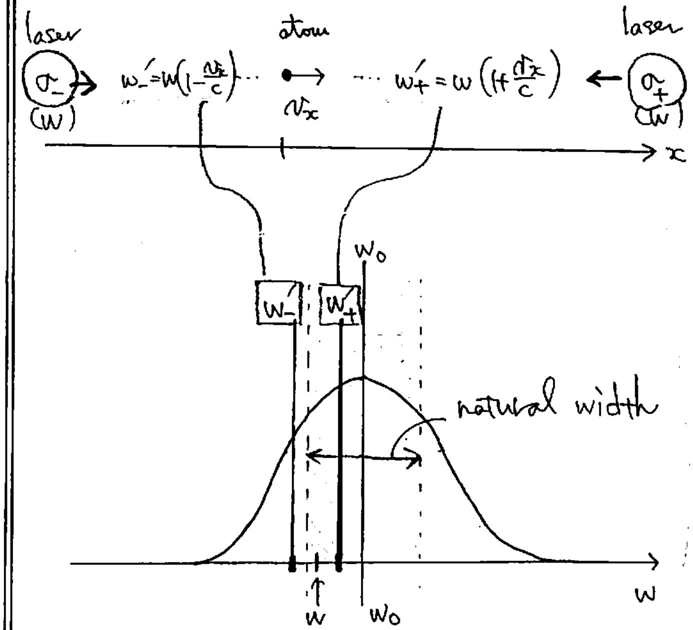
[Absorption: low energy, low entropy.
Emission: higher energy, high entropy.

Fig. 3.



光の吸収・自然放出による原子の運動量変化

Doppler shift:



※ W_+' : absorption, W_-' = ignored.

「人は自分がおかした誤謬に経験という名を与える。」
オスカー・ワイルド

(Ex.) ^{87}Rb cooling by λ_{D_2} laser.

- $v_{initial}$ = 200 m/s.
- Δv = −6 mm/s in one cycle.
- ~3.0 × 10^4 cycle (absorption, emission) is required.
- 1 cycle : within 1 μs. ⟶ stop ~ 1 m flight.

---

⑥△ 1 Applicable to all kinds of atoms ⟶ selective λ, simultaneous?

△ 2. Resolution : in principle, within atomic level.

△ 3. Laser source.

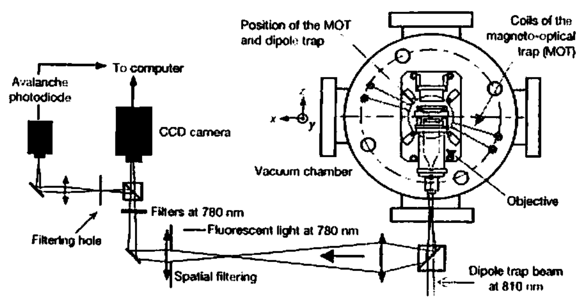
4. Single atom trap.

Sub-poissonian loading of single atoms in a microscopic dipole trap

Nicolas Schlosser, Georges Reymond, Igor Protsenko & Philippe Grangier

Laboratoire Charles Fabry de l'Institut d'Optique, UMR 8501 du CNRS, BP 147, F91403 Orsay Cedex, France

The ability to manipulate individual atoms, ions or photons allows controlled engineering of the quantum state of small sets of trapped particles; this is necessary to encode and process information at the quantum level. Recent achievements in this direction have used either trapped ions[1-3] or trapped photons in cavity quantum-electrodynamical systems[3,4]. A third possibility that has been studied theoretically[5,6] is to use trapped neutral atoms. Such schemes would benefit greatly from the ability to trap and address individual atoms with high spatial resolution.



△△ 5. Individual positioning of supercooled C, H, N, O, ensembles.

Organic molecules: simple in component, complex in structure.

☆ Target molecule of interest:

- defined structure,
- property.
- crystal packing.

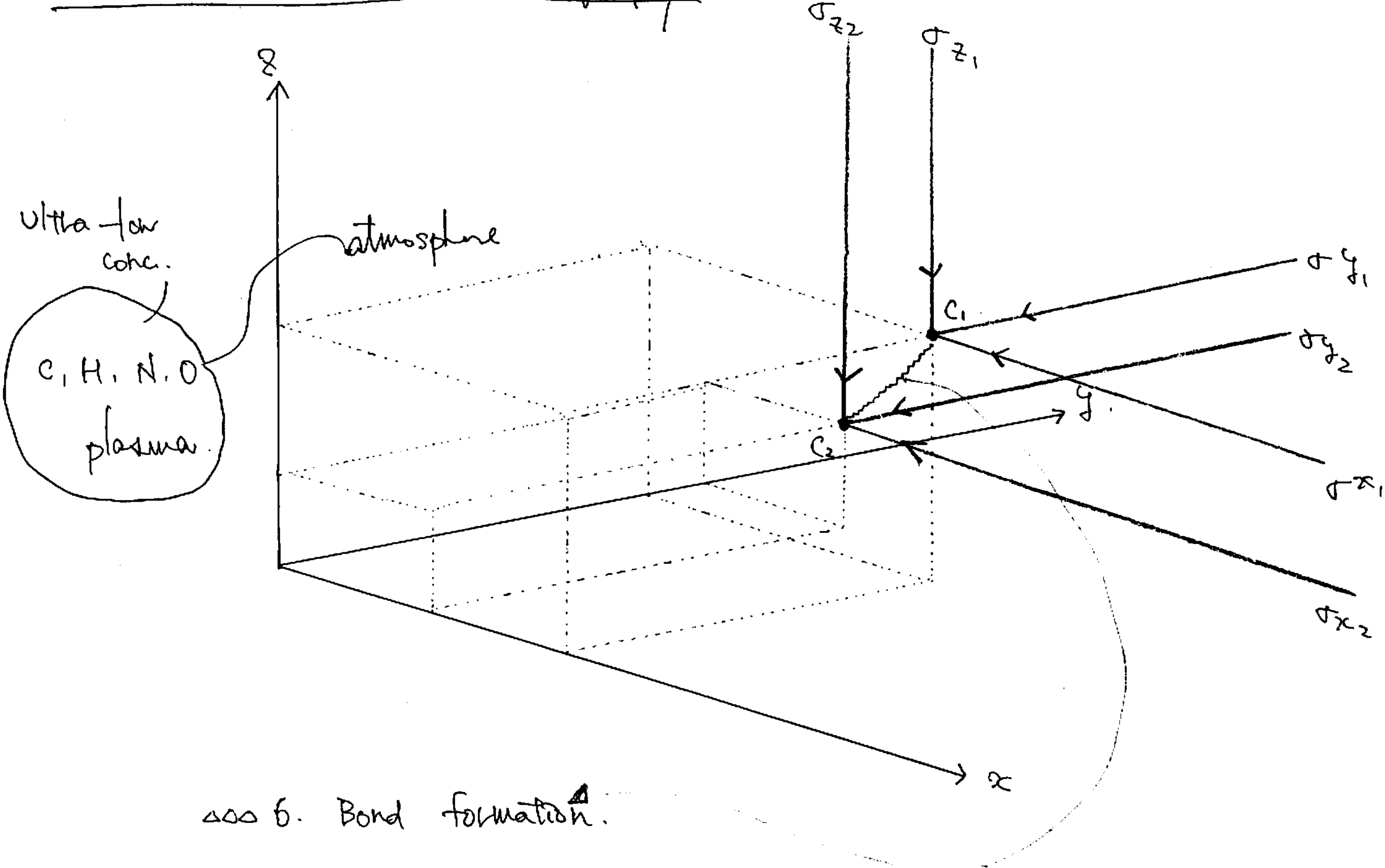
Criticism:
R. E. Smalley ⟶ K. E. Drexler

You still do not appear to understand the impact of my short piece in *Scientific American*. Much like you can't make a boy and a girl fall in love with each other simply by pushing them together, you cannot make precise chemistry occur as desired between two molecular objects with simple mechanical motion along a few degrees of freedom in the assembler-fixed frame of reference. Chemistry, like love, is more subtle than that. You need to guide the reactants down a particular reaction coordinate, and this coordinate treads through a many-dimensional hyperspace.

K. E. Drexler
computer-controlled
nano-robot.

MECHANOSYNTHETIC REACTIONS As conceived by Drexler, to deposit carbon, a device moves a vinylidenecarbene along a barrier-free path to insert into the strained alkene, twists 90° to break a pi bond, and then pulls to cleave the remaining sigma bond. COURTESY OF K. ERIC DREXLER

— Atomic Gas Laser Lithography —

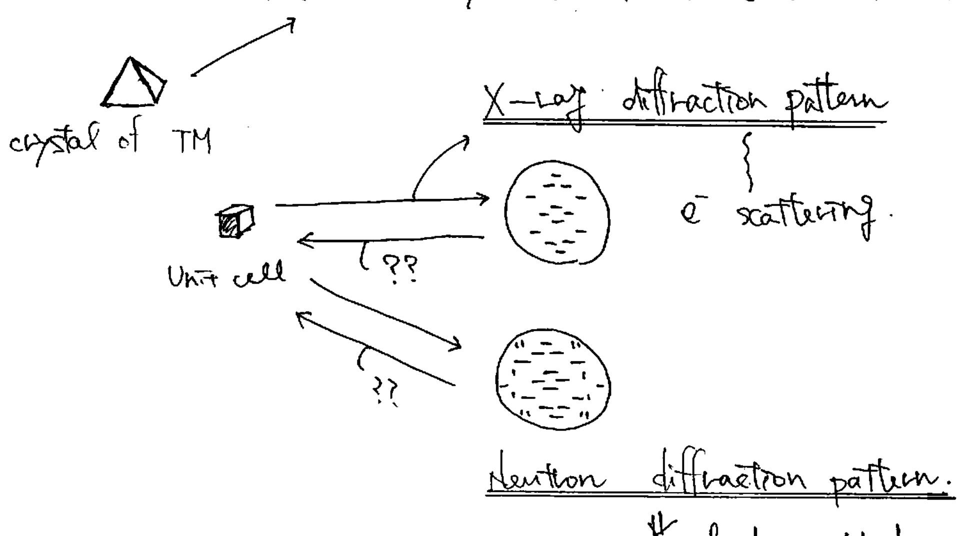


∆∆∆ 6. Bond formation.

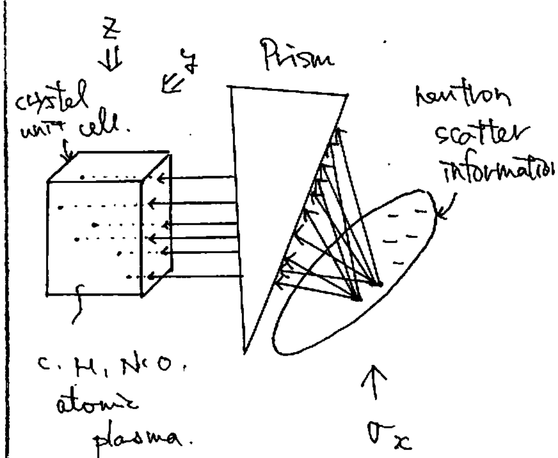
- Quantum computer: bit number ⟶ the number of different internal energy.
- Optimized position.
- 1 molecule / 1 msec ⟶ ~ 10^8 molecules / day. → xxx.

∆∆∆ 7. Integrated Atomic Gas Laser Lithography.

- Precise crystal structure is known.



∘ Mass Production in unit cell level.



「誤謬とは真理の対立物ではない、対立する真理の忘却である。」

パスカル

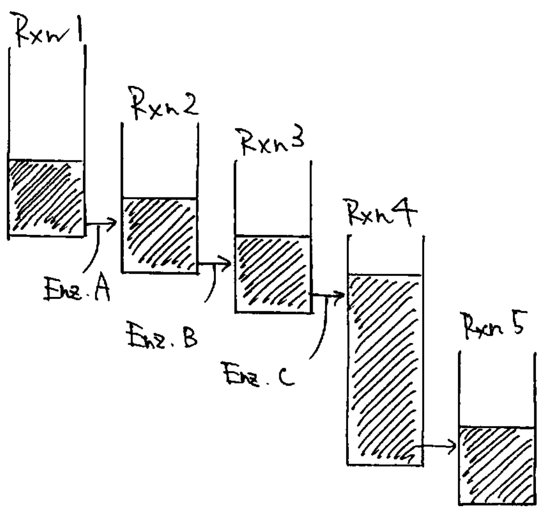
II Target Oriented Synthesis — with aquired expertise..

Goal: · Target Ⓣ

· Constant creation of Ⓣ · multiple sequence.

· input Ⓢ ⟶ ▨ ⟶ Ⓣ output.

Comparison with Biochemical Process.



• Location of each reaction.

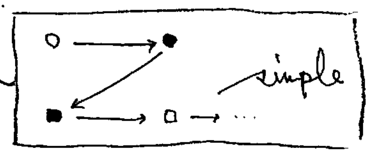
• Stationary state ⟶ Maximum work
(~~100% conv.~~)

• Non-equilibrium ↗ I. Prigogine.

High enthalpy, low entropy
⬇
Low enthalpy, high entropy
↓
integrated complexity

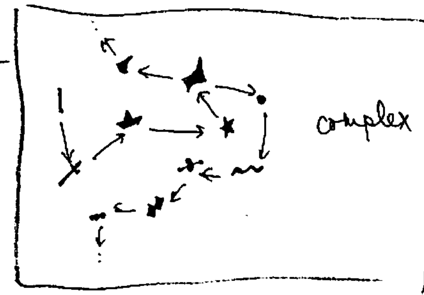
● Finite flow of reasonable {chemical / energy} transformation

keep stationary state — (maximum work, homeostasis)
↳ impose a severe limitation to the available set of stuffs..
└ thermodynamical selection.



Enzyme makes it possible to utilize
infinite set of stuffs.
└ arbitral selection ... related with enzymes.

[X ~100% conv., ~100% selectivity
[⊙ links desired stuffs one by one,
to keep the stationary state.



• Enzyme ⟷ Catalyst.

{ Enzyme : motality (← replication), keep stationary state (↑ mild..)
{ Catalyst : immortality (severe demand), toward ~100% conv. / ~100% selectivity.

$A + \hat{B} \xrightarrow{C^{*}} AB + C''$ (waste)

{ Enzyme : quasi-equilibrium continuous production.
{ Catalyst: fast one-step conversion to meet the acute demand.

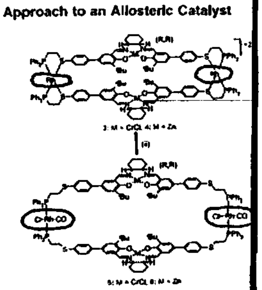
→ suitable to our goal ...

☆ • Location • Integration → Immobilized catalyst unit in flow system.

• Regulation — allosteric / Enz. synthesis / Enz. decomp. } → human control.

A Supramolecular Approach to an Allosteric Catalyst

J. AM. CHEM. SOC. 2003, 125, 10508–10509



MUCH ADO ABOUT ENZYME MECHANISMS

Studies advance understanding of how enzymes work, but some ideas provoke controversy

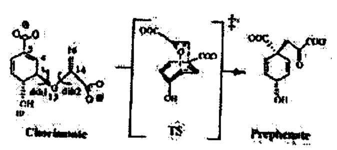
CHEMICAL & Engineering News
February 23,2004
Volume 82, Number 8
CENEAR 82 8 pp. 35-39

• Stabilization of TS ... too much simplified ...

The near attack conformation approach to the study of the chorismate to prephenate reaction

Sun Hur and Thomas C. Bruice*
Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106

PNAS | October 14, 2003 | vol. 100 | no. 21 | 12015–12020



Scheme 1.

$$S \underset{\text{ground state}}{\overset{\Delta G_N^{\circ}}{\rightleftharpoons}} NAC \xrightarrow{\Delta G_{TS}^{\ddagger}} [TS] \quad [1]$$

$$\Delta G^{\ddagger} = \Delta G_N^{\circ} + \Delta G_{TS}^{\ddagger} \quad [2]$$

(experimental) (calculated)

Table 1. Free energies of experimental $\Delta G^{\ddagger}$ and computational ΔG_N° (kcal/mol)

	$\Delta G^{\ddagger}$	−	ΔG_N°	=	$\Delta G_{TS}^{\ddagger}$
Water	24.2		8.1		16.1
1F7	21.3		5.5		15.8
R90Cit	21.2		4.1		17.1
E52A	18.2		1.3		16.9
w-BsCM	15.4		0.3		15.1
w-EcCM	15.2		0.1		15.1

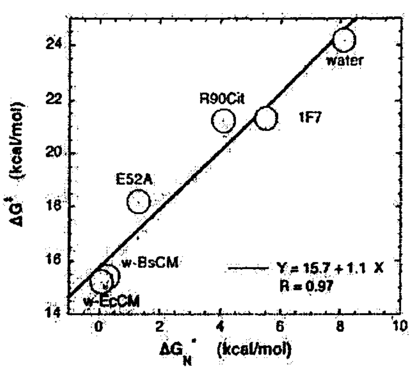


Fig. 8. Plot of $\Delta G^{\ddagger}$ vs. ΔG_N° in Table 1. Circles are of 1 kcal/mol diameter. The equation at the bottom right is the linear fit equation for the six data points. *R* is the correlation coefficient for the linear fit.

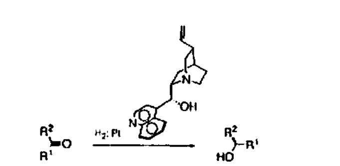
• $\Delta G_{TS}^{\ddagger}$: nearly same.
• $\Delta G^{\ddagger}$ — ΔG_N° proportional.

Origins of Enantioselectivity in Reductions of Ketones on Cinchona Alkaloid Modified Platinum

Grigoriy Vayner,[†] K. N. Houk,[*,†] and Y.-K. Sun[*,‡]

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, and Merck & Co., Inc., P.O. Box 2000, Rahway, New Jersey 07065

J. AM. CHEM. SOC. 2004, 126, 199–203



	% ee
R^1=Me R^2= CO_2Et	97[1a]
R^1=Me R^2= $CH(OMe)_2$	96[1d]
R^1=Ph R^2= CF_3	92[1]
R^1=Me R^2=CH(OMe)CH_3	95[1a]
R^1, R^2= alkyl or aryl	<40[5]

Figure 1. Asymmetric ketone reduction on cinchonidine-modified Pt.

covalent bond.

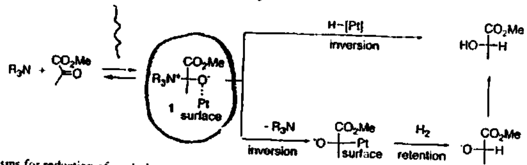


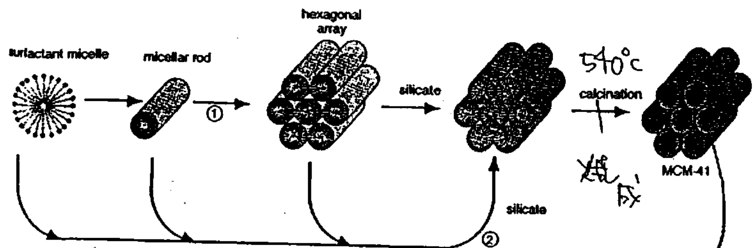
Figure 3. Postulated mechanisms for reduction of methyl pyruvate catalyzed by cinchonidine-modified Pt (R_3N = cinchonidine). Besides the C–Pt covalent bond shown there is an interaction between the oxygens and the quinoline of cinchonidine with the Pt surface.

(a)

· Localized reaction units.

· Mesoporous material

20 – 500 Å pore size



mobile catalyst molecular sieves

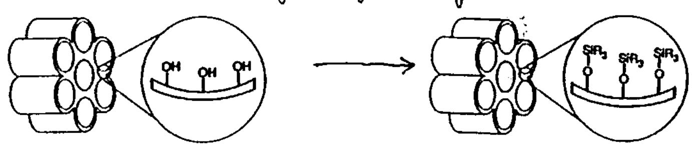
• Pore size: 16 Å – >100 Å

• Specific surface area : >1000 m²/g

Functionalization.

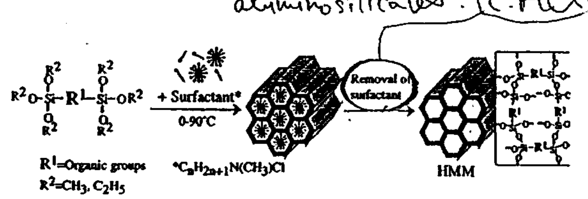
Post-synthetic modification

· coating , grafting.



Pre-synthetic modification.

· organo-functionalized aluminosilicates. (c.HCl)



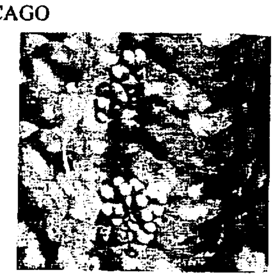
CHIRAL CATALYSIS AT SURFACES

Researchers probe promising heterogeneous catalysts with potential for industrial applications

MITCH JACOBY, C&EN CHICAGO

CHEMICAL & Engineering News

March 15, 2004
Volume 82, Number 11



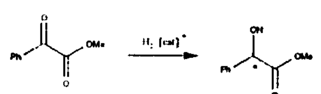
ACE IN THE HOLE Confining a rhodium(I) organometallic catalyst (bottom molecule) within a silica pore restricts the possible orientations of a reactant molecule (methyl benzoylformate) on approach to the catalyst, thereby boosting enantioselectivity.
COURTESY OF ROBERT RAJA

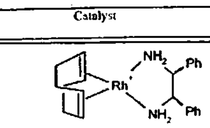
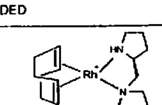
Enantioselective heterogeneous catalysis has not yet made a big splash in industrial chemistry. Researchers are fascinated by the molecular subtleties that drive asymmetric conversions. And chemical manufacturers are keen to exploit the potential benefits offered by the catalytic systems. As mechanistic studies continue to reveal additional details of the systems' inner workings, asymmetric surface chemistry moves toward large-scale application.

Constraining Asymmetric Organometallic Catalysts within Mesoporous Supports Boosts Their Enantioselectivity

Robert Raja,[*,‡] John Meurig Thomas,[*,‡,§] Matthew D. Jones,[‡] Brian F. G. Johnson,[‡] and David E. W. Vaughan[‖]

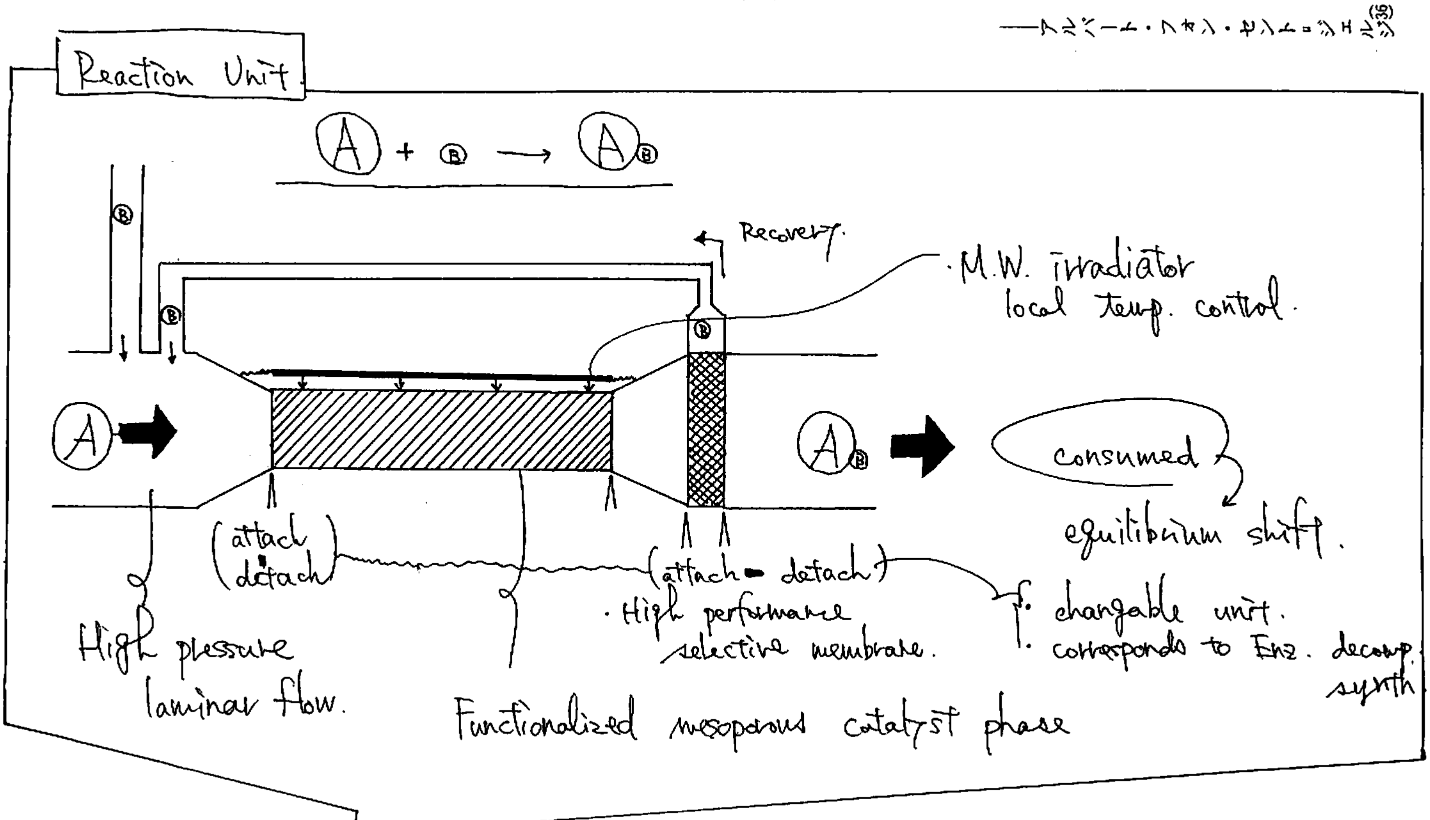
J. AM. CHEM. SOC. 2003, 125, 14982–14983

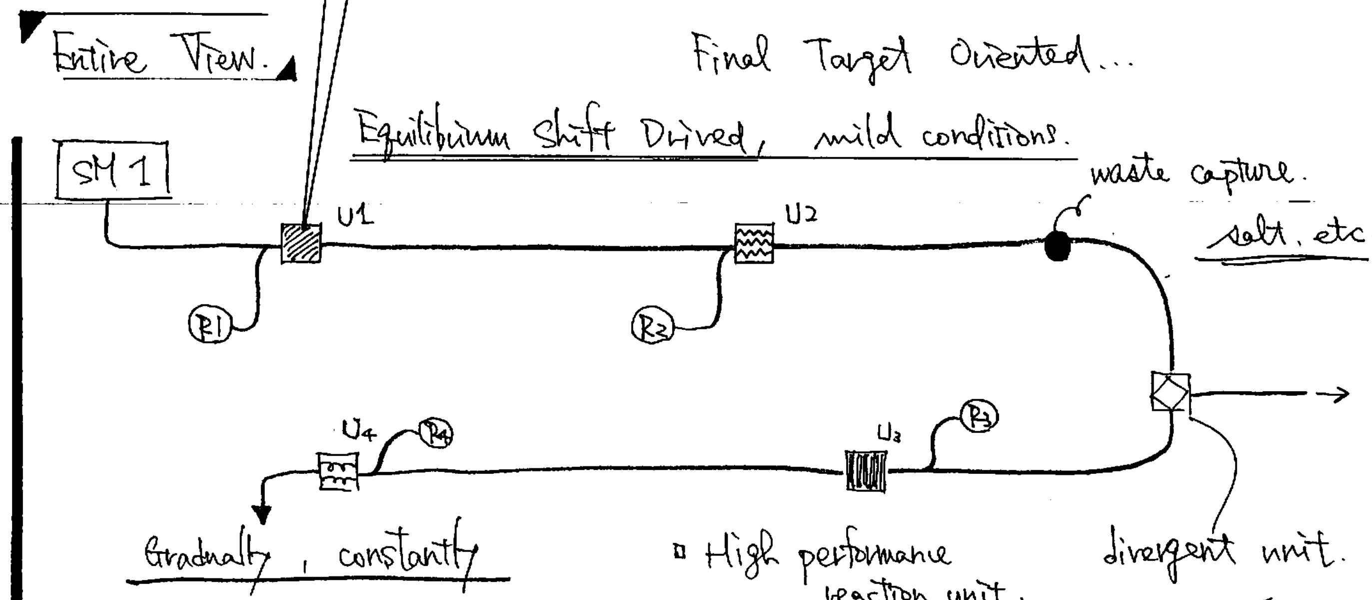


Catalyst	Counter-ion	Catalyst	Silica Type (pore dimension)	Metal	t (h)	Conv.[b]	TOF[d] (h^{-1})	ee[c]
 Rh(COD)DED	$CF_3SO_3^-$	Homogeneous	-	Rh(I)	2.0	69.9	60	0[f]
	$CF_3SO_3^-$	Heterogeneous	Davison 923 (38 Å)	Rh(I)	0.5	77.7	596	50
					2.0	98.1	188	79
			Davison 634 (60 Å)		0.5	59.7	458	68
					1.0	75.5	290	73
			Davison 654 (250 Å)		0.5	38.8	298	0
					2.0	83.1	159	4
 Rh(COD)PMP	$CF_3SO_3^-$	Homogeneous	-	Rh(I)	0.5	46.2	145	53
	$CF_3SO_3^-$	Heterogeneous	Davison 923 (38 Å)	Rh(I)	0.5	92.8	643	85
					2.0	95.8	166	94
			Davison 634 (60 Å)		0.5	63.0	436	72
					2.0	91.5	159	78
			Davison 654 (250 Å)		0.5	60.7	420	65
					2.0	86.9	151	59

Synthesis and characterisation of heterogeneous catalysts.

The triflate salt (50 mgs) was dissolved in CH_2Cl_2 (20 ml), to which dry silica (500 mgs) was added to form a slurry. This was left stirring at room temperature for three hours, during which time the solid took on the colour of the rhodium complex and the solution became pale. The solution was filtered and the silica was washed with copious amounts of CH_2Cl_2 until the washings were colourless. The catalyst was then dried *in-vacuo* and isolated as a pale yellow solid.





▫ High performance
reaction unit.
· No more : ~~fast~~, ~~100%~~ rxn.
· mild, selective

· Target of each step is defined.

⇓

"custom – made Reactor"

≈

Catalytic Antibody,
and related...

A: Oxidation with O_2,
Reduction with H_2.
Substitution with R–OH.

Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex

Jaime A. Pool, Emil Lobkovsky & Paul J. Chirik

Department of Chemistry and Chemical Biology, Baker Laboratory Cornell University, Ithaca, New York 14853, USA

Nature 2004, 427, 527.

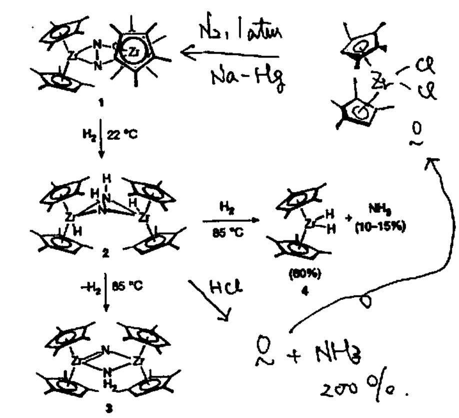
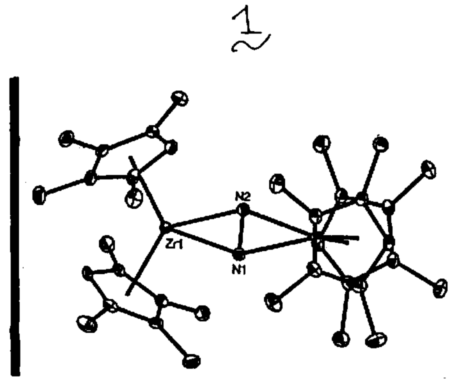
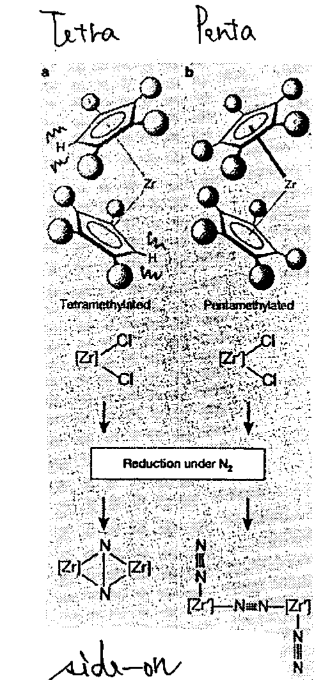


Figure 1 Hydrogenation and cleavage of N_2.





A non-metal system for nitrogen fixation

Yoshiaki Nishibayashi*, Makoto Saito*, Sakae Uemura*, Shin-ichi Takekuma†, Hideko Takekuma†, Zen-ichi Yoshida†

1 + $Na_2S_2O_4$ (100 eq.) —(1 atm N_2, light, 60°C, 1h)→ NH_3 33%

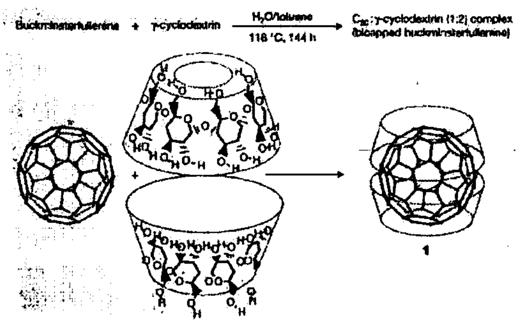


Figure 1 Preparation of γ-cyclodextrin–bicapped C_{60} complex (1), which is used in the fixation of nitrogen to ammonia. A mixture of C_{60} (0.400 g; 0.555 mmol) and γ-cyclodextrin (1.200 g; 0.925 mmol) was stirred in a water (160 ml)/toluene (60 ml) mixture at 118 °C for 48 h and then γ-cyclodextrin (0.600 g; 0.463 mmol) was added twice more every 48 h; complex 1 was produced in 70% yield (1.464 g; 0.391 mmol) as a purple solid, with each molecule being coordinated with 24 H_2O molecules (stoichiometry from thermogravimetric and differential thermal analysis). In the fixation reaction, a suspension of 1 (37.4 mg; 0.010 mmol) under 1 atmosphere of nitrogen with $Na_2S_2O_4$ (174 mg; 1.00 mmol) in water (10 ml) was magnetically stirred at 60 °C for 1 h under visible light from a fluorescent lamp. The yield of ammonia was quantified by using indophenol reagent.

Direct allylic substitution of allyl alcohols by carbon pronucleophiles in the presence of a palladium/carboxylic acid catalyst under neat conditions

Nitin T. Patil and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan

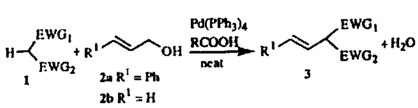


Table 2. Pd(PPh₃)₄/acetic acid catalysed allylic substitution of allyl alcohols with C-nucleophiles under neat conditions

Entry	1	2	Pd(PPh₃)₄ (mol%)	Conditions	Product 3	Yield[a] (%)
1	1a	2b	2	80 °C/30 min	3b	81
2	COOEt / COOEt, 1b	2a	5	100 °C/10 min	3c	95
3	1b	2b	5	100 °C/10 min	3d	61[b]
4	COPh / SO₂Ph, 1c	2a	2	80 °C/1.5 h	3e	95
5	1c	2b	2	80 °C/1.5 h	3f	63[c]
6	COPh / COOEt, 1d	2a	5	100 °C/2 h	3g	98
7	1d	2b	5	100 °C/2 h	3h	94
8	COPh / COOEt, 1e	2a	5	100 °C/5 h	3i	85
9	1f	2a	0.5	80 °C/30 min	3j	71[d]
10	COOEt, 1g	2a	2	100 °C/10 min	3k	98
11	1g	2b	2	80 °C/15 min	3l	96

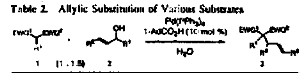
[a] Isolated yield.
[b] 30% of diallylated product was isolated.
[c] 21% of diallylated product was isolated.
[d] Yield refers to diallylated product.

ORGANIC LETTERS
2003
Vol. 5, No. 18
3241–3244

Palladium-Catalyzed, Carboxylic Acid-Assisted Allylic Substitution of Carbon Nucleophiles with Allyl Alcohols as Allylating Agents in Water

Kei Manabe and Shū Kobayashi*

Table 2. Allylic Substitution of Various Substrates



entry	1	2	Pd(PPh₃)₄ (mol %)	conditions	product	yield[a] (%)
1	1b	2a	5	reflux, 5 h	3b	90
2	1c	2a	2	reflux, 10 min	3c	92
3	1d	2a	2	reflux, 10 min	3d	76
4	1e	2a	5	reflux, 1 h	3e	78
5[b]	1f	2a	2	80 °C, 1.5 h	3f	>99
6[c]	1g	2a	0.5	80 °C, 30 min	3g	74[d]
7	1a	2b	5	80 °C, 30 min	3h	73
8	1h	2c	5	80 °C, 20 min	3i	93
9	1a	2d	5	80 °C, 2 h	3j	80[e]
10[b]	1a	2e	5	reflux, 30 min	3k	66

[a] Isolated yield. [b] Molar ratio of 1:2 is 1:1.1. [c] Molar ratio of 1:2 is 1:2.2. [d] Product was diallylated compound 3g. [e] Containing regioisomer 4 (4% yield).