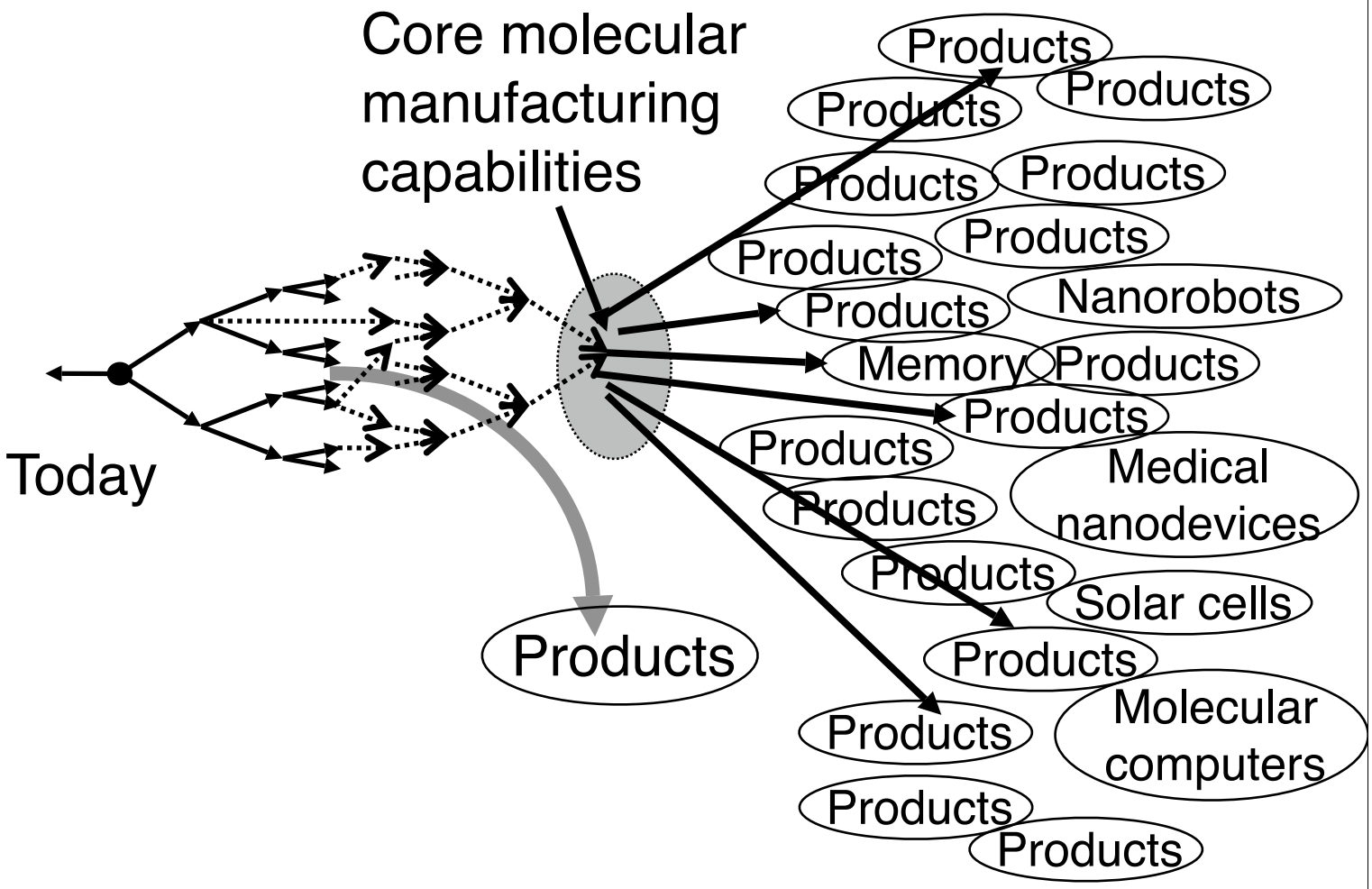
The contributions of Robert Freitas to molecular nanotechnology

Ralph C. Merkle

Institute for Molecular Manufacturing and

Nanofactory Collaboration

Overview


Core molecular manufacturing capabilities
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Nanorobots
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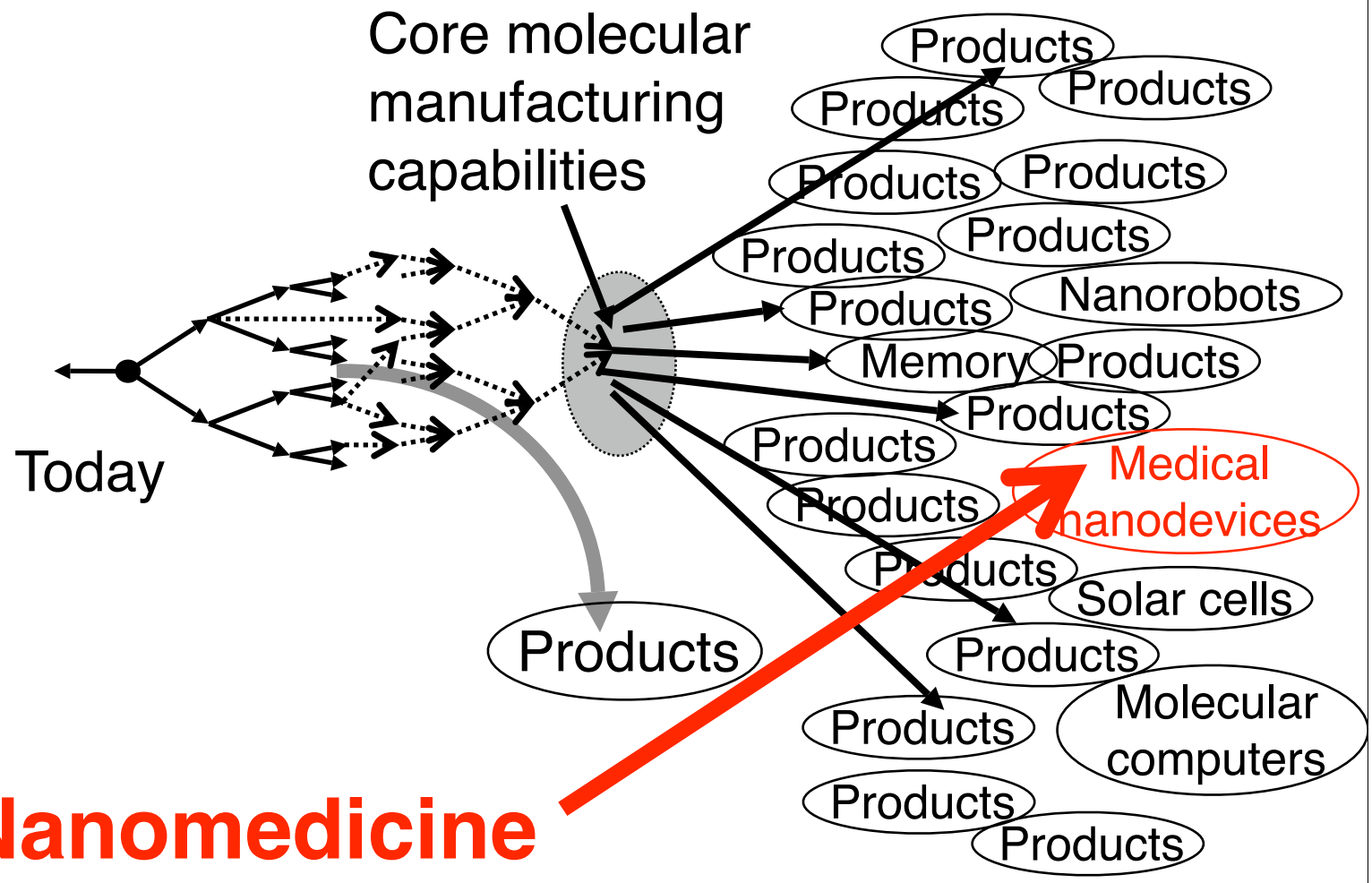
Overview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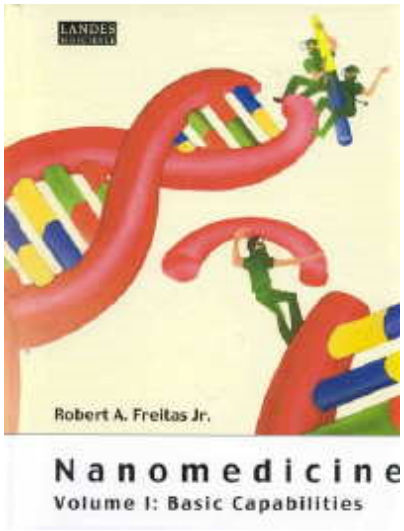
Nanomedicine

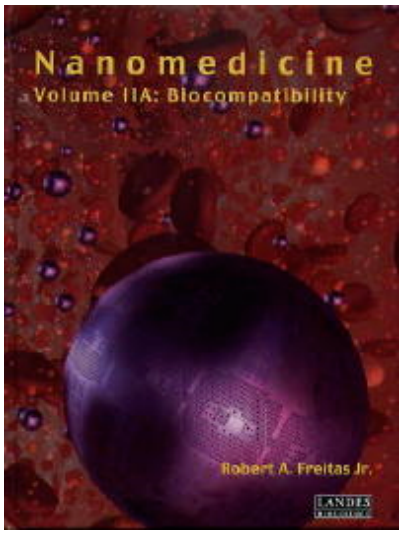
Nanomedicine



Nanomedicine, Vol. I: Basic Capabilities
(Landes Bioscience, 1999)

Nanosensors, nanoscale scanning
Power (fuel cells, other methods)
Communication
Navigation (location within the body)
Manipulation and locomotion
Computation
and more

www.nanomedicine.com



Nanomedicine, Vol. IIA: Biocompatibility
(Landes Bioscience, 2003)

Cell response to diamond surfaces
Nanorobot immunoreactivity
Phagocyte avoidance and escape
Nanorobotic mechanical vasculopathies

and much, much more

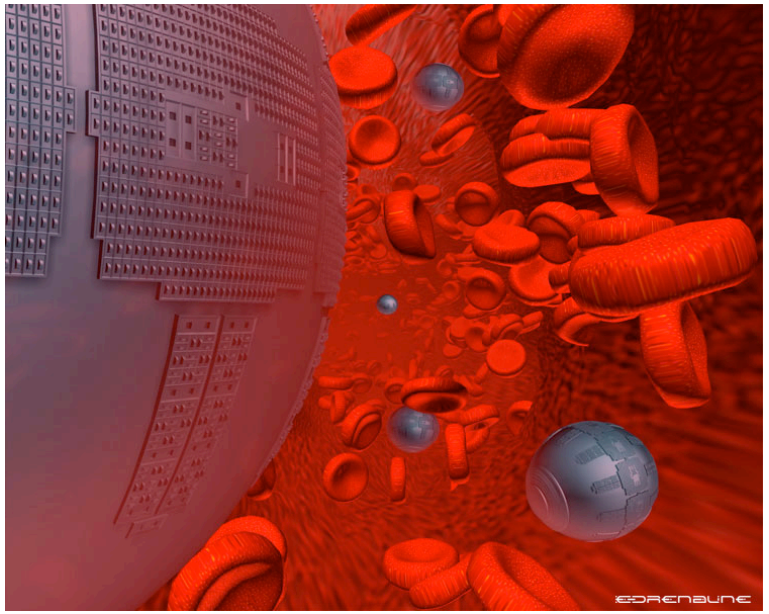
www.nanomedicine.com

Supply oxygen

Exploratory Design in Medical Nanotechnology: A Mechanical Artificial Red Cell

Artificial Cells, Blood Substitutes, and Immobil. Biotech. **26**(1998):411-430,

by Robert A. Freitas Jr.

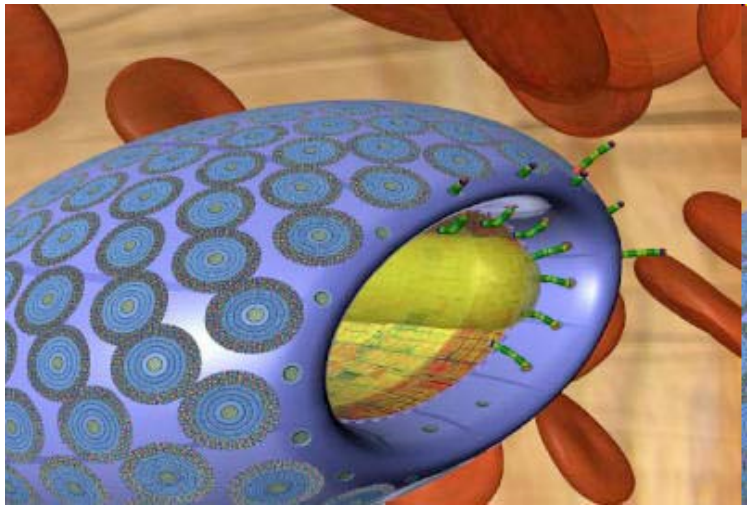


Digest bacteria

Microbivores: Artificial Mechanical Phagocytes using Digest and Discharge Protocol

J. Evol. Technol. 14(April 2005):55-106

by Robert A. Freitas Jr.



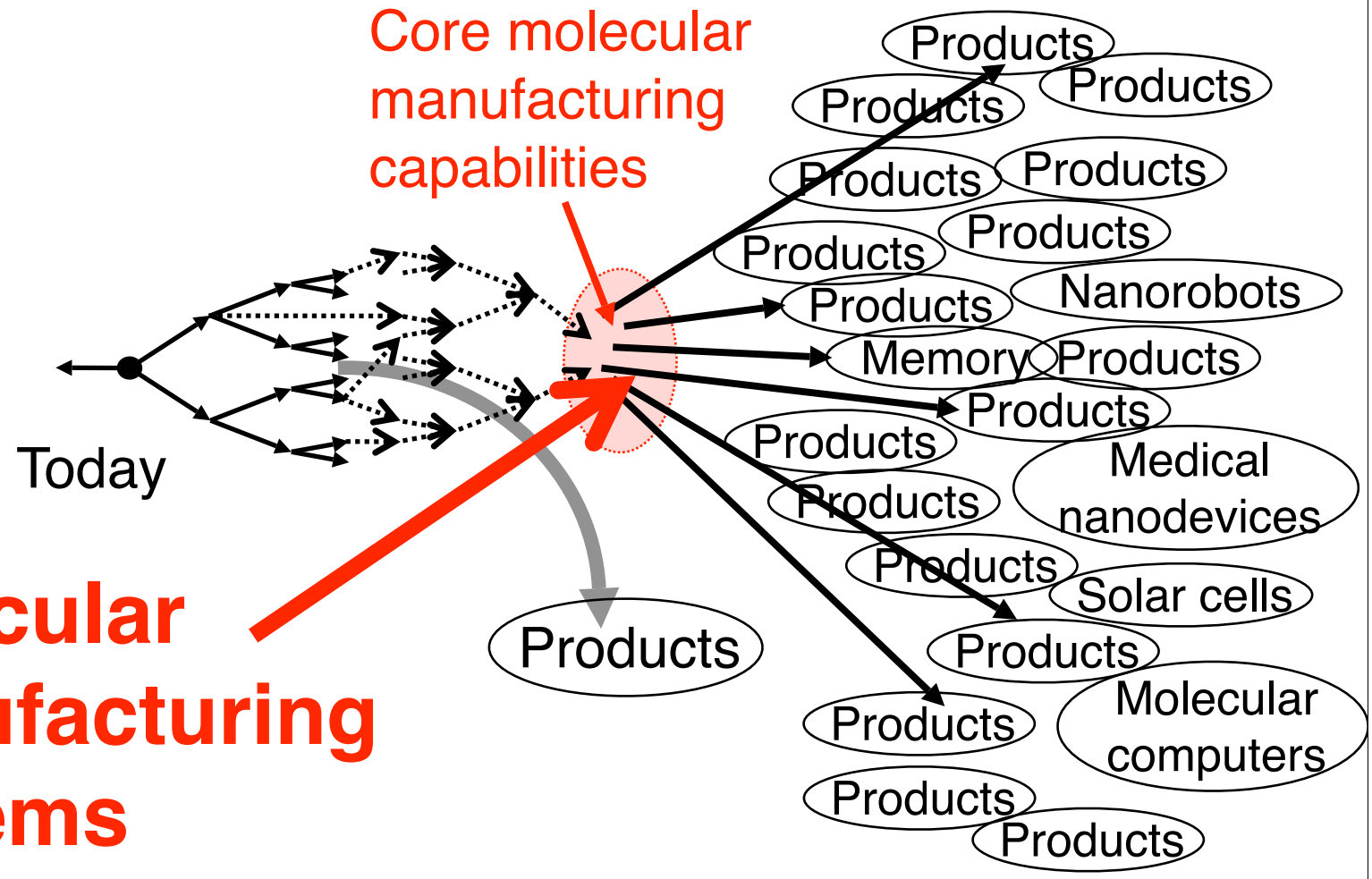
Replace chromosomes

The Ideal Gene Delivery Vector: Chromallocytes, Cell Repair Nanorobots for Chromosome Replacement Therapy

J. Evol. Technol. 16(June 2007):1-97

by Robert A. Freitas Jr.

Overview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Products
Molecular manufacturing systems

Self replication

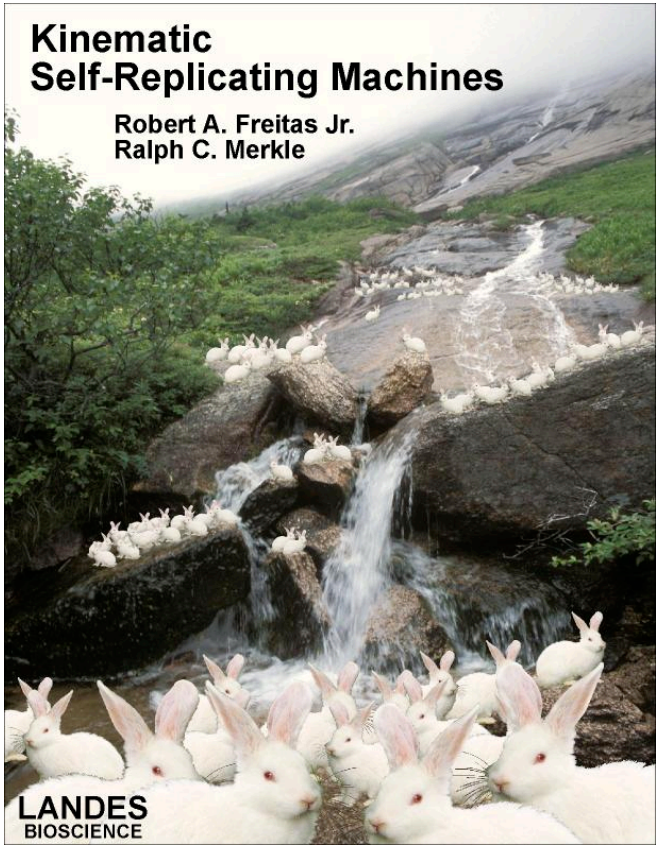
Advanced Automation for Space Missions
(NTIS, 1982)

Robert A. Freitas Jr.
and William P. Gilbreath, Eds.

Final Report of the 1980 NASA/ASEE sponsored study of self-replicating lunar factories.

http://www.islandone.org/MMSG/aasm/

Self replication



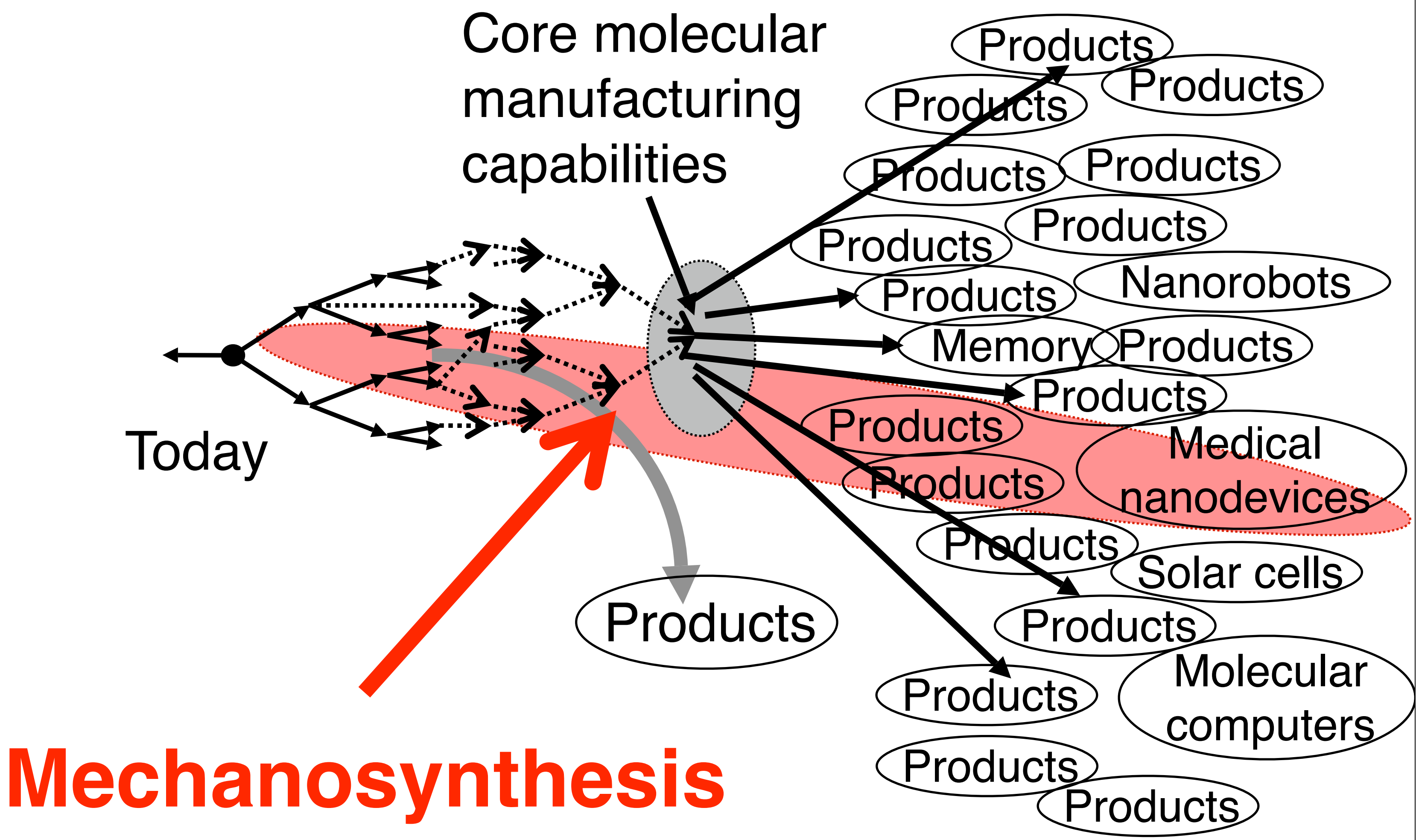
Kinematic Self-Replicating Machines
(Landes Bioscience, 2004)

By Robert A. Freitas Jr. and Ralph C. Merkle

Reviews the voluminous theoretical and experimental literature about physical self-replicating systems.

www.molecularassembler.com/KSRM.htm

Overview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Molecular
computers
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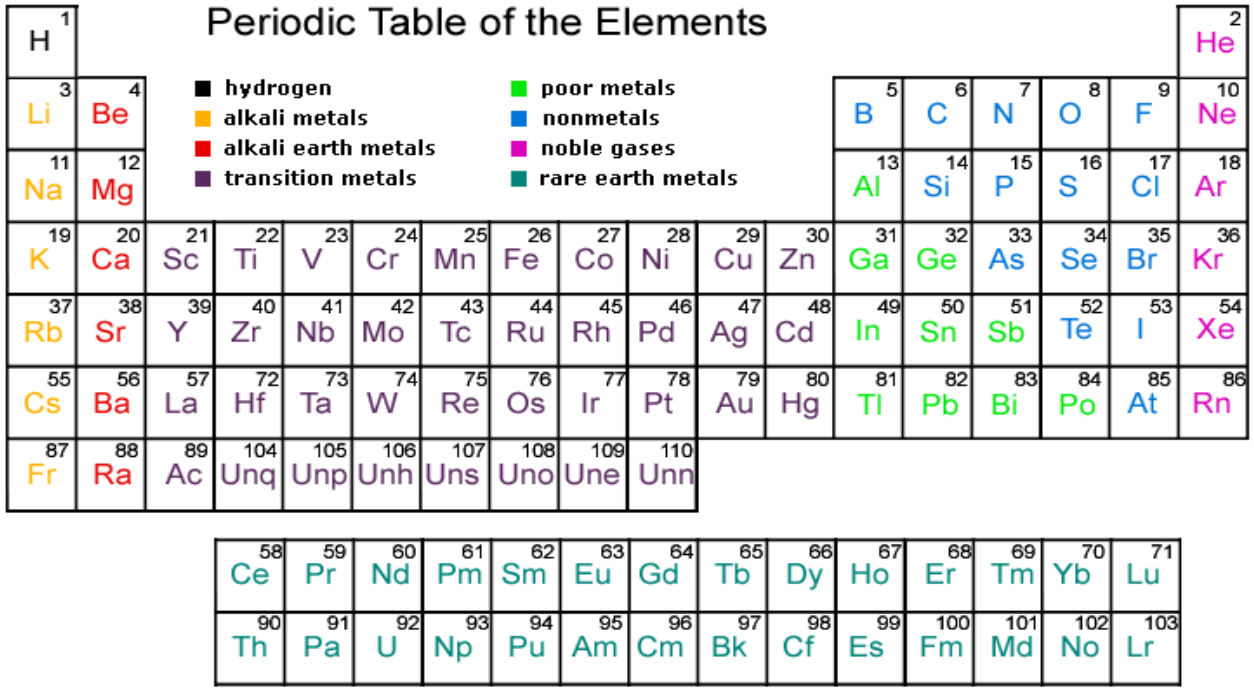
Products
Mechanosynthesis

The goal

Inexpensively arrange the elements in almost any atomically precise structure consistent with physical law

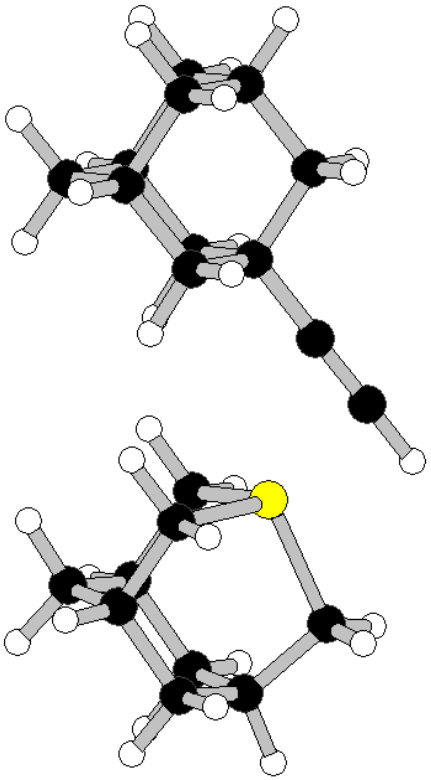


Three elements: H, C, Ge

Fewer elements makes the problem easier to analyze and easier to do

H and **C** can build almost any rigid structure (diamond, lonsdaleite, graphite and graphene, carbon nanotubes and fullerenes, polyynes, other hydrocarbons)

Ge provides “just enough” synthetic flexibility



A Minimal Toolset for Positional Diamond Mechanosynthesis

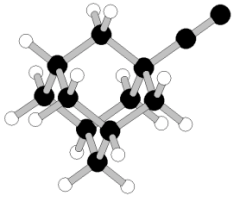
Journal of Computational and Theoretical Nanoscience Vol.5, 760–861, 2008

by Robert A. Freitas Jr.

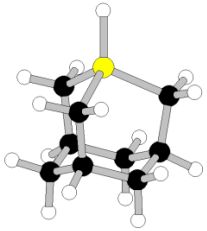
and Ralph C. Merkle

Bibliography of over 50 references on mechanosynthesis at http://www.molecularassembler.com/Nanofactory/AnnBibDMS.htm

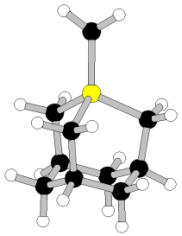
Molecular tools



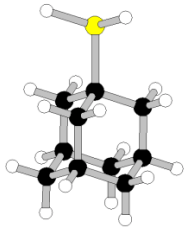
HAbst



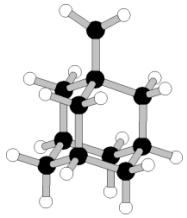
HDon



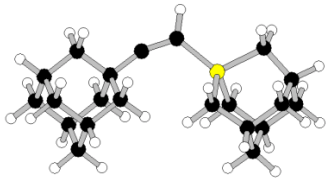
GM



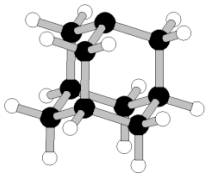
Germylene



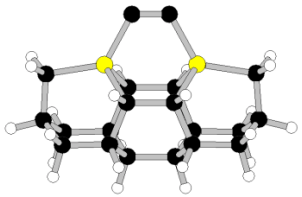
Methylene



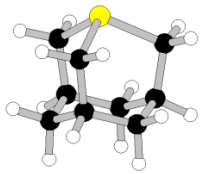
HTrans



AdamRad



DimerP



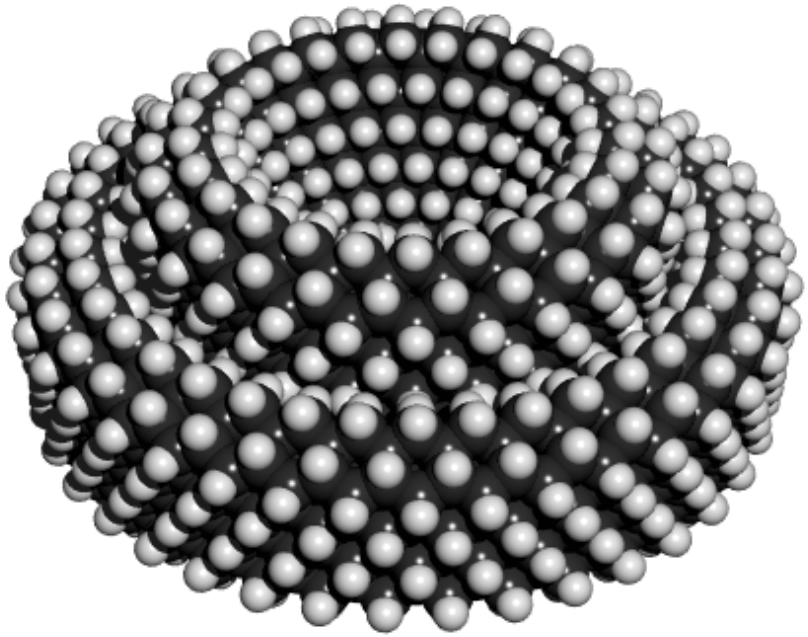
GeRad

What they could make

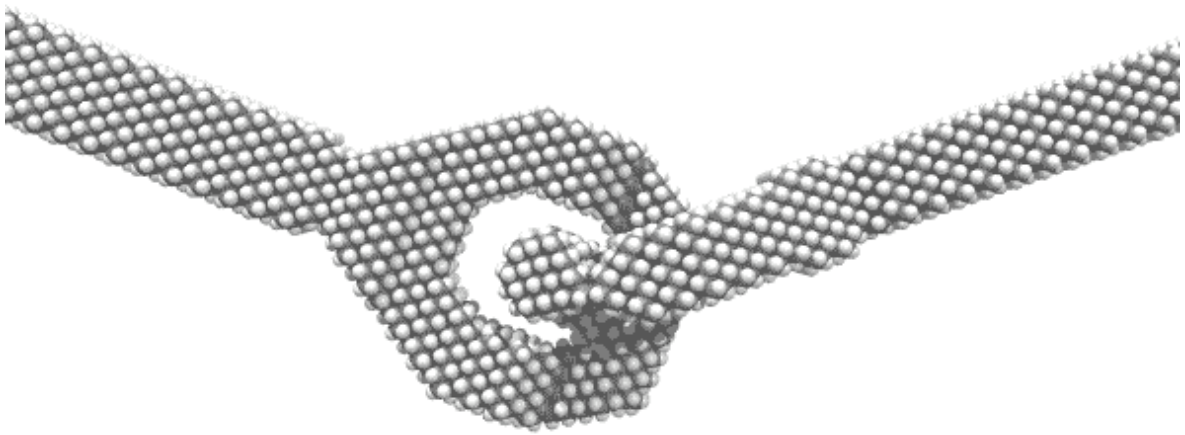
Diamond physical properties

Property	Diamond's value	Comments
Chemical reactivity		Extremely low
Hardness (kg/mm2)	9000	CBN: 4500 SiC: 4000
Thermal conductivity (W/cm-K)	20	Ag: 4.3 Cu: 4.0
Tensile strength (pascals)	3.5×10^9 (natural)	10^{11} (theoretical)
Compressive strength (pascals)	10^{11} (natural)	5×10^{11} (theoretical)
Band gap (ev)	5.5	Si: 1.1 GaAs: 1.4
Resistivity (W-cm)	10^{16} (natural)	
Density (gm/cm3)	3.51	
Thermal Expansion Coeff (K-1)	0.8×10^{-6}	SiO2: 0.5×10^{-6}
Refractive index	2.41 @ 590 nm	Glass: 1.4 - 1.8
Coeff. of Friction	0.05 (dry)	Teflon: 0.05

Hydrocarbon bearing



Hydrocarbon universal joint



Molecular robotic arm

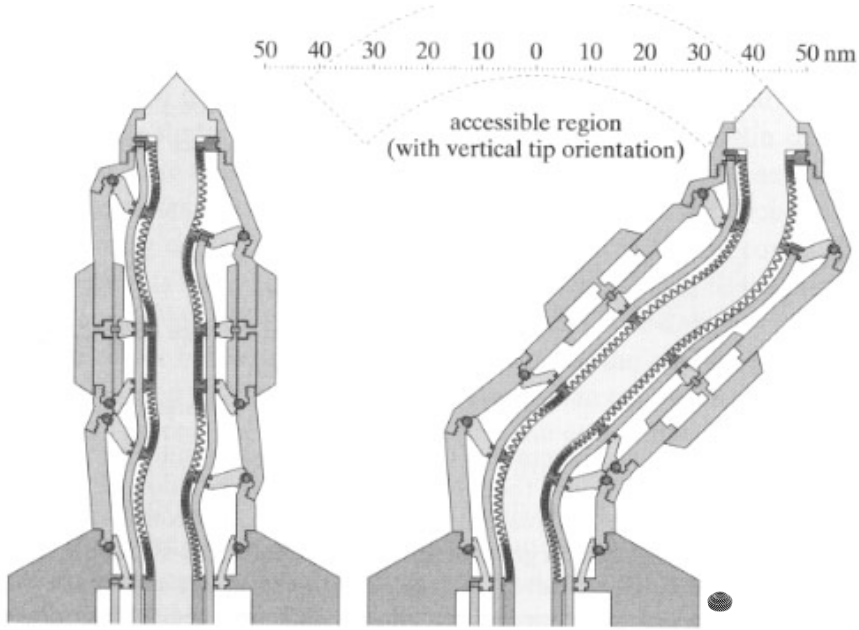


Figure 13.14. Cross section of a stiff manipulator arm, showing its range of motion (schematic).

Making diamond today

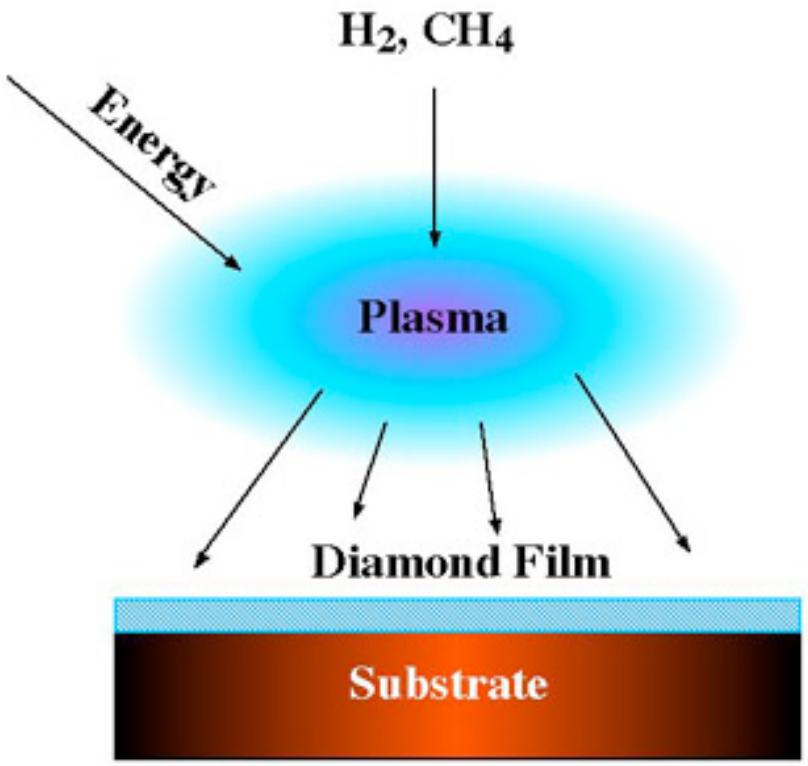
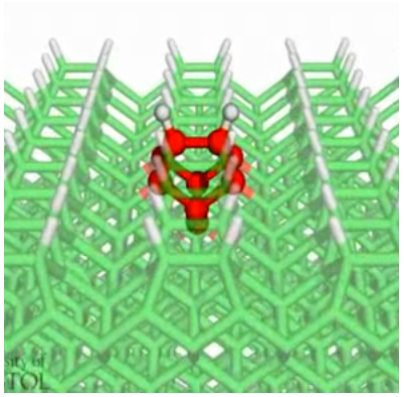
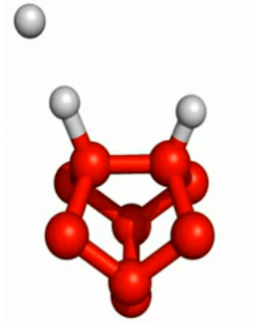
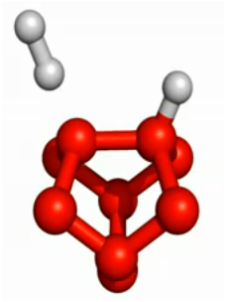


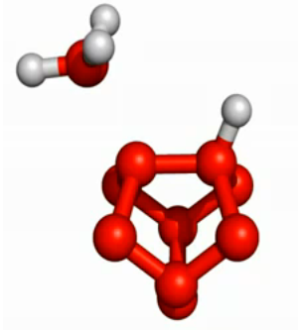
Illustration courtesy of P1 Diamond Inc.

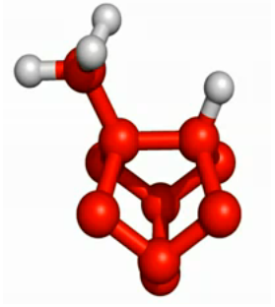
Diamond growth



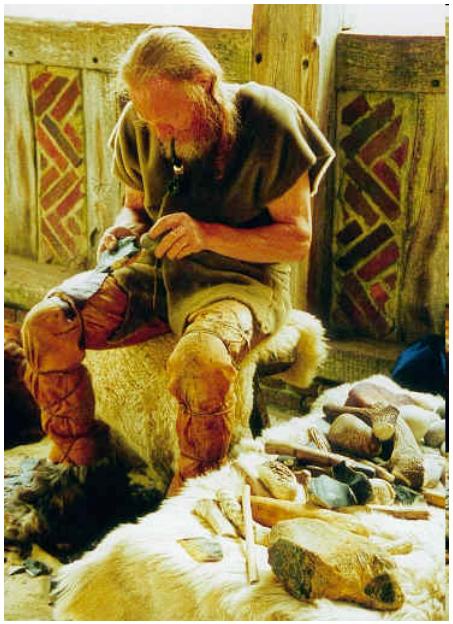


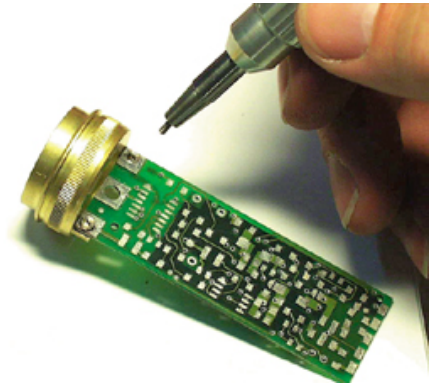






Positional assembly





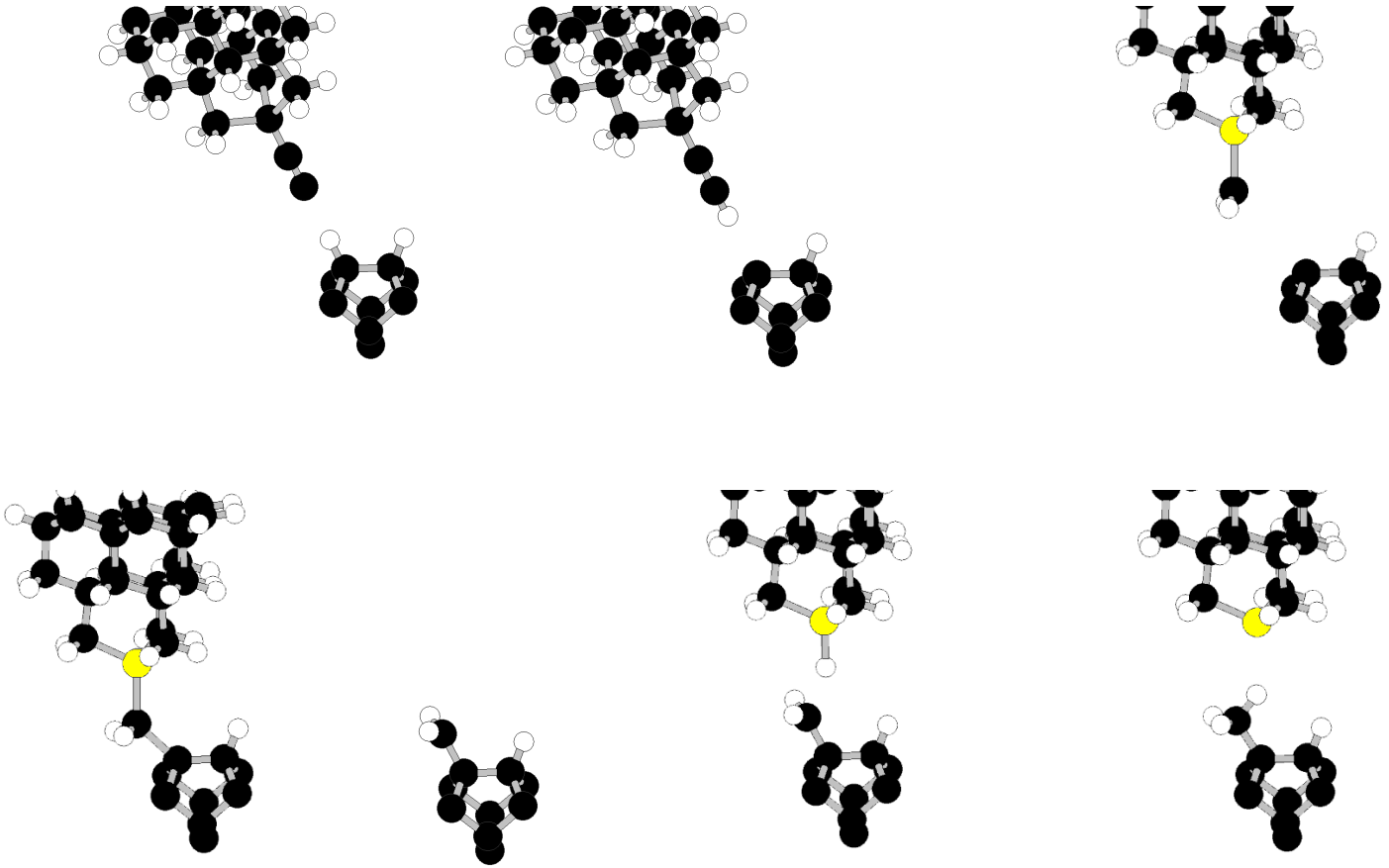
A strategy for the synthesis of diamondoid structures

Positional assembly (6 degrees of freedom)

Highly reactive compounds (radicals, carbenes, etc)

Inert environment (vacuum) to eliminate side reactions

Positional assembly



Computational methods

1630 tooltip/workpiece structures

65 Reaction Sequences

328 reaction steps

354 unique pathological side reactions

1321 reported energies

consuming 102,188 CPU-hours (using 1-GHz CPUs)

Computational methods

Gaussian 98

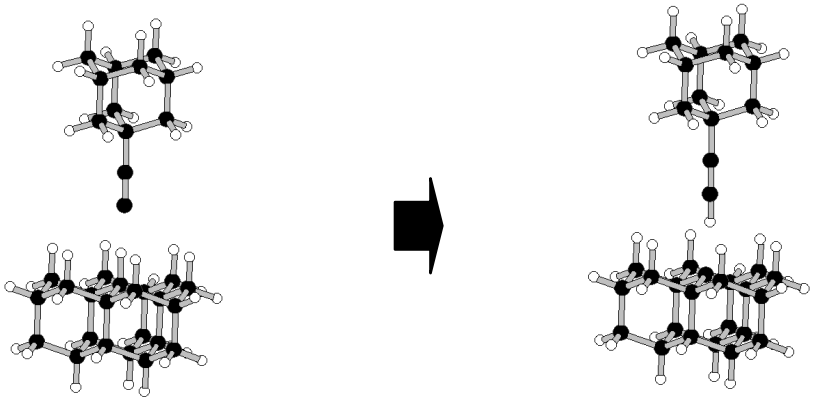
Singlet or doublet geometries optimized with no constrained degrees of freedom using spin-unrestricted Hartree-Fock (UHF) analysis at the B3LYP/3-21G* level of theory

Single point energy calculations performed at the B3LYP/6-311 +G(2d,p) level of theory

The mean absolute deviation from experiment (MAD) for B3LYP/ 6-311+G(2d,p) // B3LYP/3-21G* energies is estimated as 0.14 eV for carbon-rich molecules

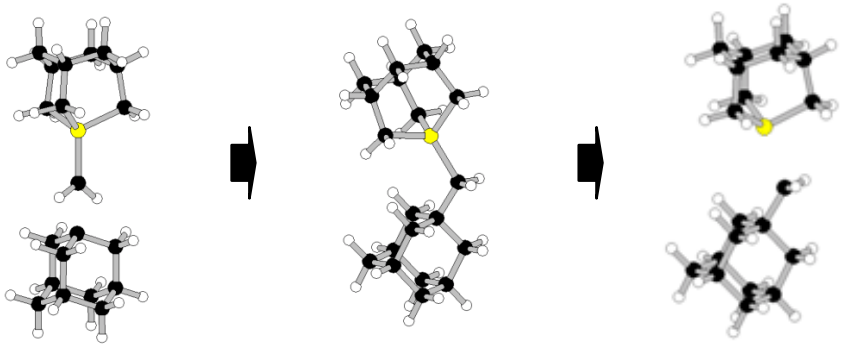
Barriers of 0.4 eV against side reactions in most cases

H abstraction



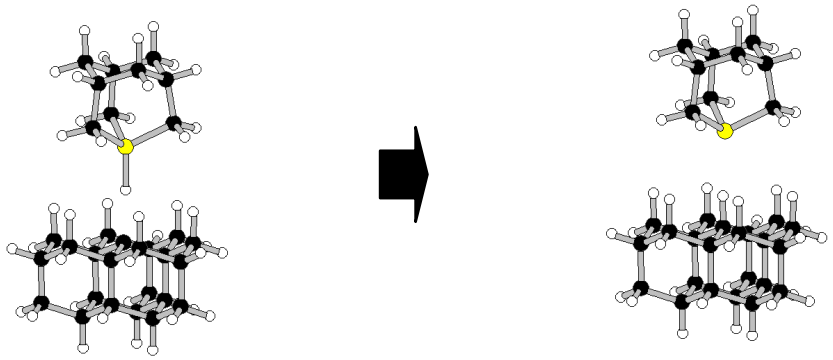
Hydrogen abstraction from a C(111) surface, creating a radical site.
-1.59 eV

C placement



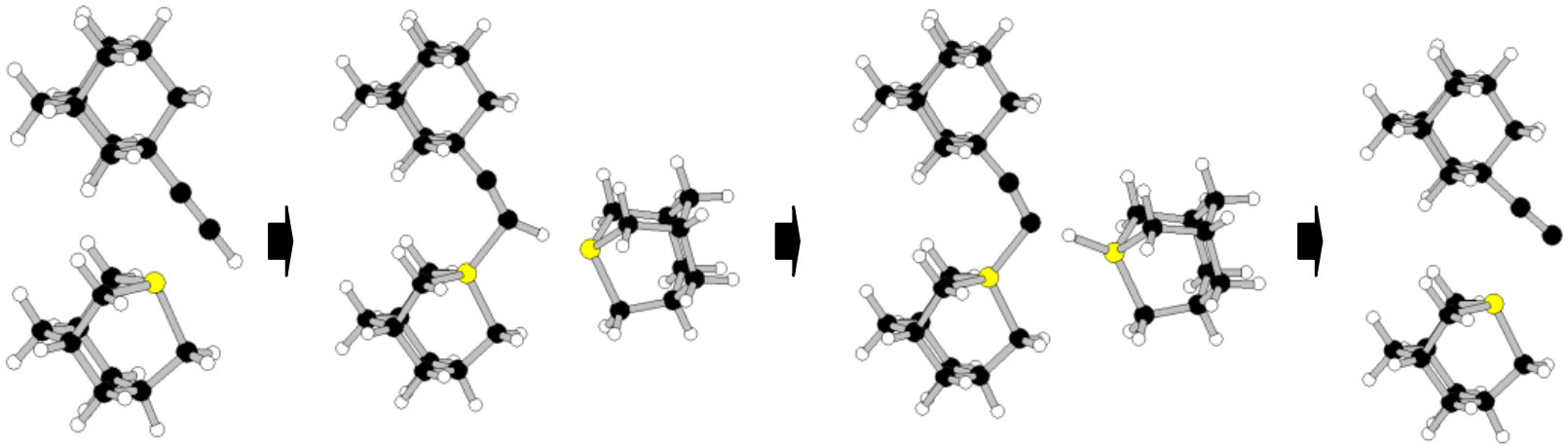
C placement on C(111) using GM tool
C radical addition to C radical -3.17 eV
GeRad removal +2.76 eV (note Ge-C bond is “soft”)

H donation



Hydrogen donation onto a C(111) surface radical.
-0.61 eV

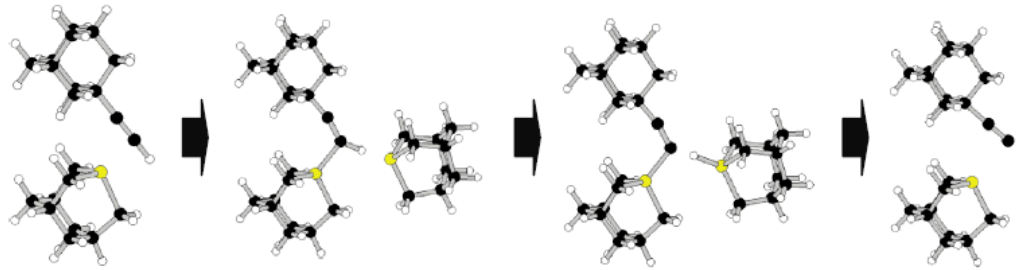
H recharge



Recharging HAbst and HDon

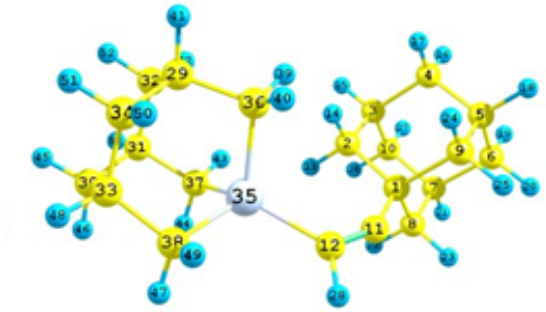
H recharge

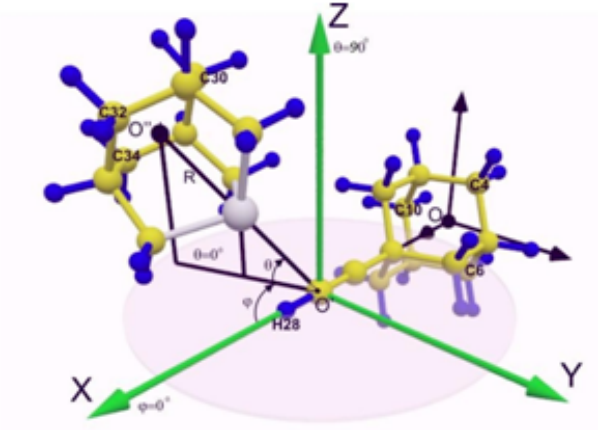
	Step 1	Step 2	Step 3	



Step	Description of Reaction	Mult.	Ener. (eV)	Barr. (eV)
1	**Join GeRad tool to apical C atom of HAbstH tool**			
	R: HAbstH (ACC0A/28) + GeRad (ACC0A/25)	S + D		
	P: C15FCcis (ACC0A/53) [≡**HTrans tool**]	D	**−0.43** [a]	
	T: Barrier map minimum from Tarasov et al. (2007)			**+0.10** [b]
	P: C15FCtrans (ACC0A/53)	D	−0.55	
	R: CH33Ge (ACC0A/13) + ClusterHAbH (ACC0A/16)	D + S		
	T: R1415Trans-QST3 (ACC1A/29)	D		**+0.27** [b]
1B1	H steal from HAbstH workpiece to GeRad tool			
	R: HAbstH (ACC0A/28) + GeRad (ACC0A/25)	S + D		
	P: HAbst (ACC0A/27) + HDon (ACC0A/26)	D + S	+2.19	
1D1	H migrates to radical site from adjacent CH in chain on HTrans			
	R: C15FCcis (ACC0A/53)	D		
	P: C15FCp2 (ACC0A/53)	D	−0.13	
	T: C15FCp2TS (ACC1A/53)	D		+1.66
1F6	H dissociates from -C●=CH- group on HTrans tool			
	R: S15cis (ACC0A/11)	D		
	P: S16Run0 (ACCCA/10) + H (ACC0A/1)	S + D	+2.68	
2	**Abstract apical H from HAbstH using GeRad tool**			
	R: S15cis (ACC0A/11) + GeRad (ACC0A/25)	D + D		
	P: S16Run0 (ACCCA/10) + HDon (ACC0A/26)	S	**−0.83** [cd]	
	R: S15trans (ACC0A/11) + GeRad (ACC0A/25)	D + D		
	P: S16Run0 (ACCCA/10) + HDon (ACC0A/26)	S	**−0.84** [c]	
2F6	H dissociates from GeRad handle of HDon tool			
	P: HDon (ACC0A/26)	S		

H recharge



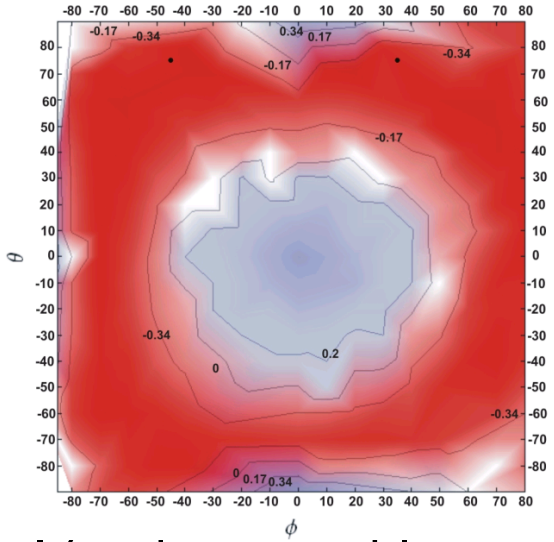


Optimal Tooltip Trajectories in a Hydrogen Abstraction Tool Recharge Reaction Sequence for Positionally Controlled Diamond Mechanosynthesis

Denis Tarasov, Natalia Akberova, Ekaterina Izotova, Diana Alisheva, Maksim Astafiev, Robert A. Freitas Jr.

Journal of Computational and Theoretical Nanoscience, 6 (2009).

H recharge



PES for Reaction I (endoergic = blue, exoergic = red, energy in eV) as a function of tooltip positional angles ϕ = -180° to +180°, θ = -90° to +90°, at tooltip separation distance R = 4.85 Å and GeRad rotational angle ρ = +40°, with labeled isoergic contours. Energy minima are marked with solid dots at (ϕ, θ) = (-46°, +74°) (-0.506 eV) and (+34°, +74°) (-0.504 eV) at R = 4.85 Å, (ϕ, θ) = (-23°, +26°) (-0.486 eV) and (+24°, +26°) (-0.482 eV) at R = 4.35 Å.

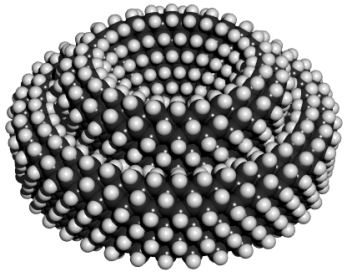
Reaction summary

- Abstract hydrogen with HAbst
- Donate hydrogen with HDon
- Recharge HAbst and HDon
- Add carbon to workpiece with GM tool
- Recharge GM tool (see paper)
- Tool synthesis sequences (see paper)

Tool properties

Starting from small feedstock molecules, a set of tools can:

make another set of tools
recharge all tools
make stiff hydrocarbon nanorobotic devices



Molecular robotic arm

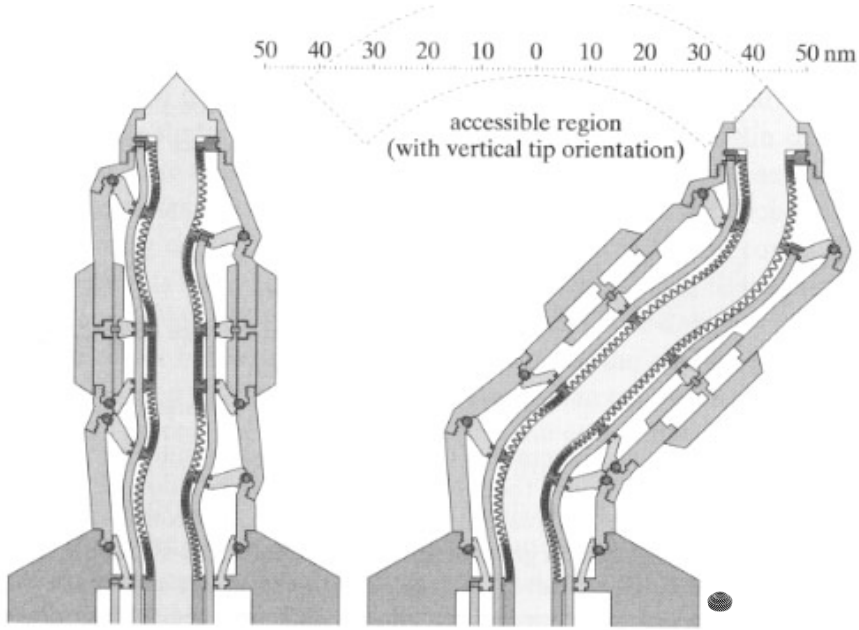
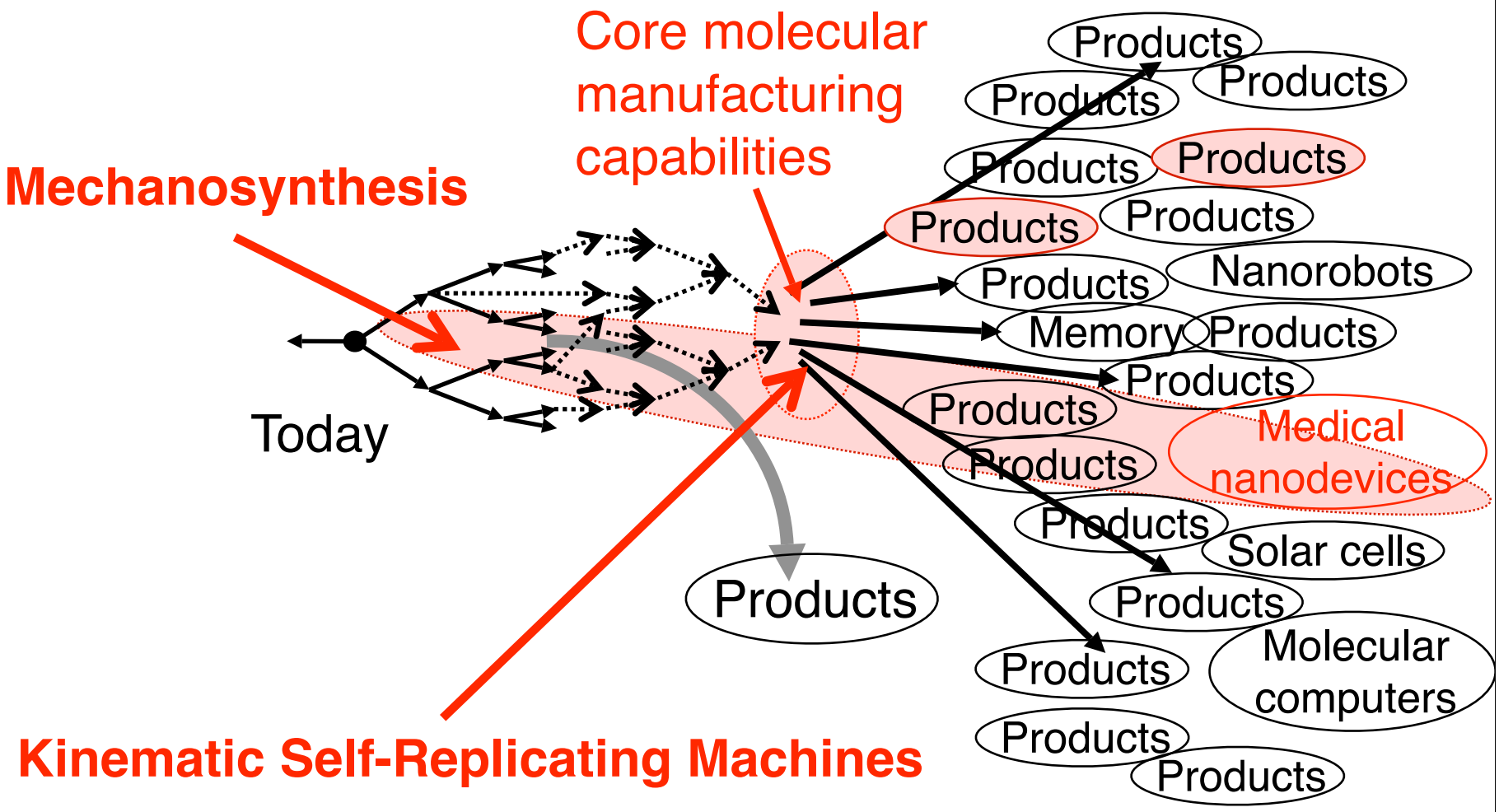


Figure 13.14. Cross section of a stiff manipulator arm, showing its range of motion (schematic).

Contributions of Robert Freitas

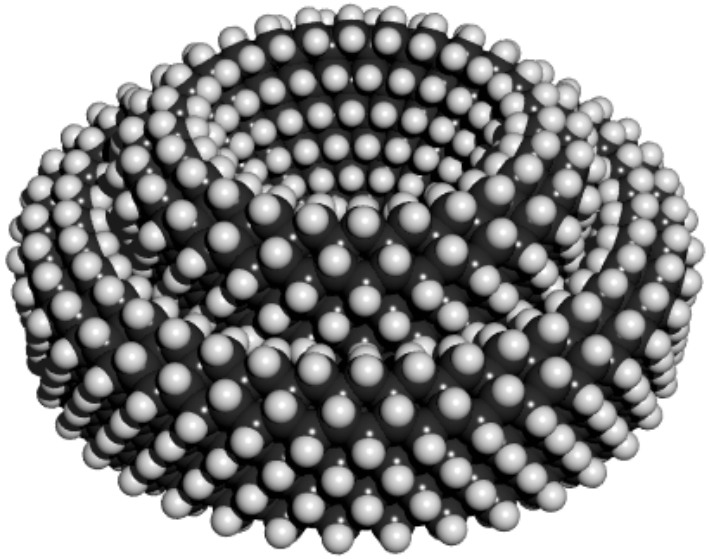


End of talk

Bearings

Sliding surfaces can run dry
    "lubricant" would not fit
No wear
it either breaks or doesn't
Superlubricity – *really* slippery

Hydrocarbon bearing

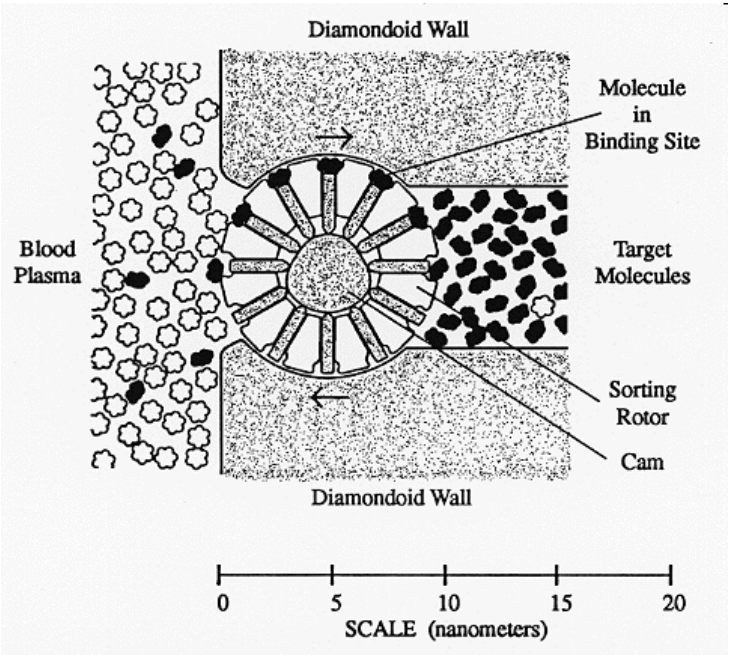


m = 13, n = 20, period = 1/260
Barrier to rotation (barrier between one minima and the next) is less than 0.004 kcals/mol

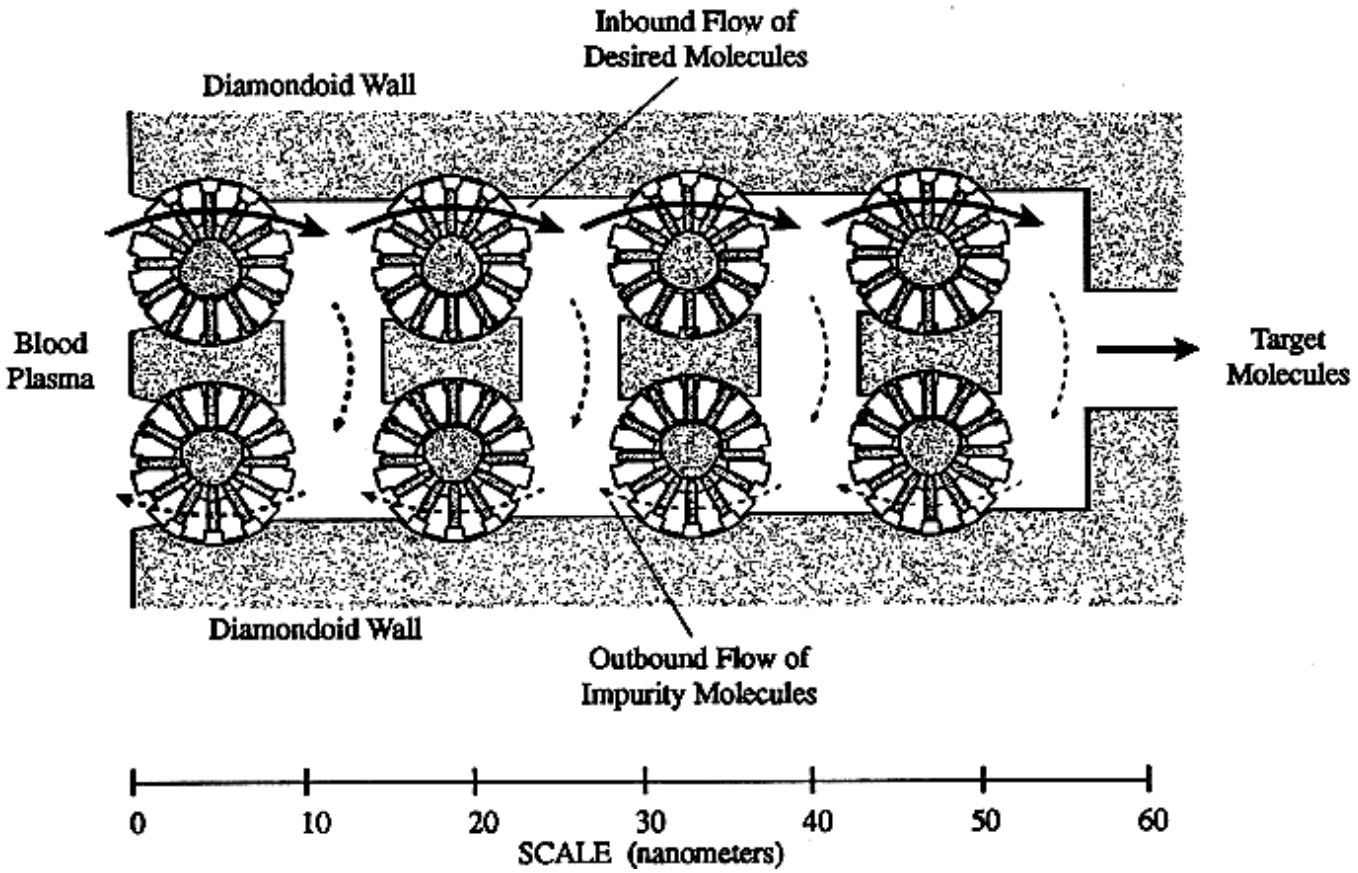
http://www.zyvex.com/nanotech/bearingProof.html

Uptake of feedstock

Sorting rotors for selective uptake and purification of feedstock molecules

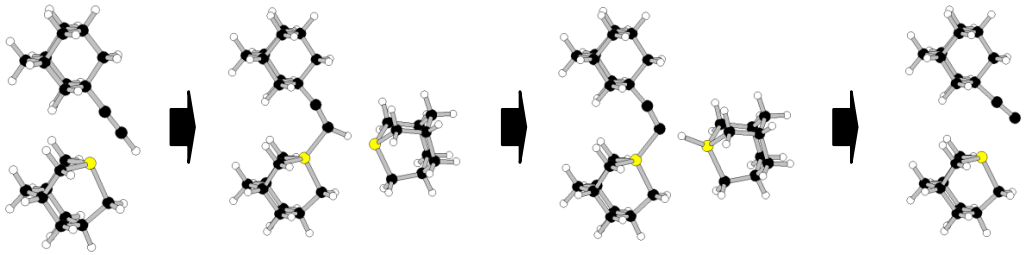


Uptake of feedstock



Multistage cascade for high purity from industrial grade raw materials

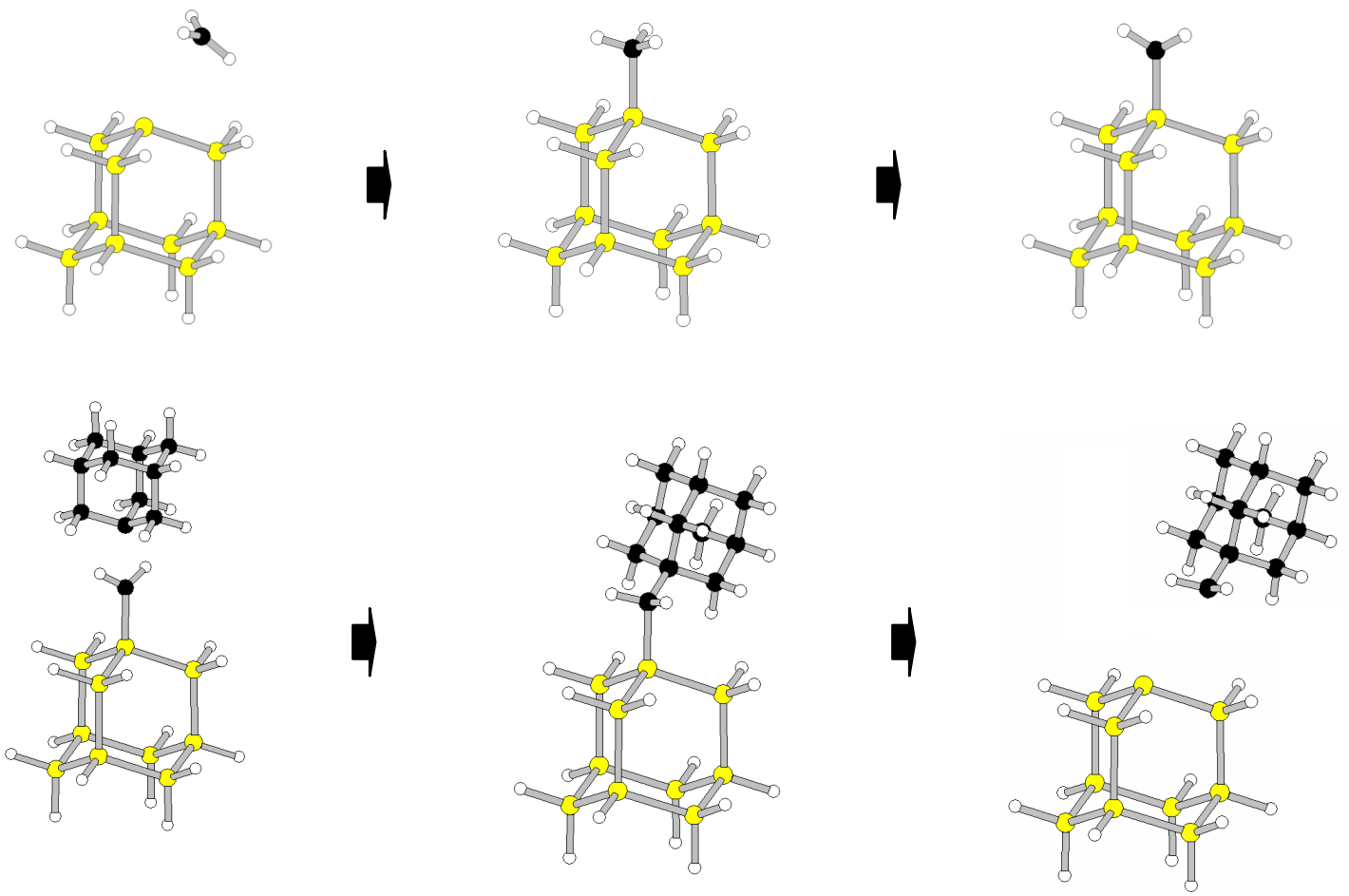
H recharge



Recharging HAbst and HDon
(initial approach of first GeRad optimized by Tarasov et al (2007), -0.43 eV with -0.1 eV barrier)

Second GeRad abstraction -0.83 eV

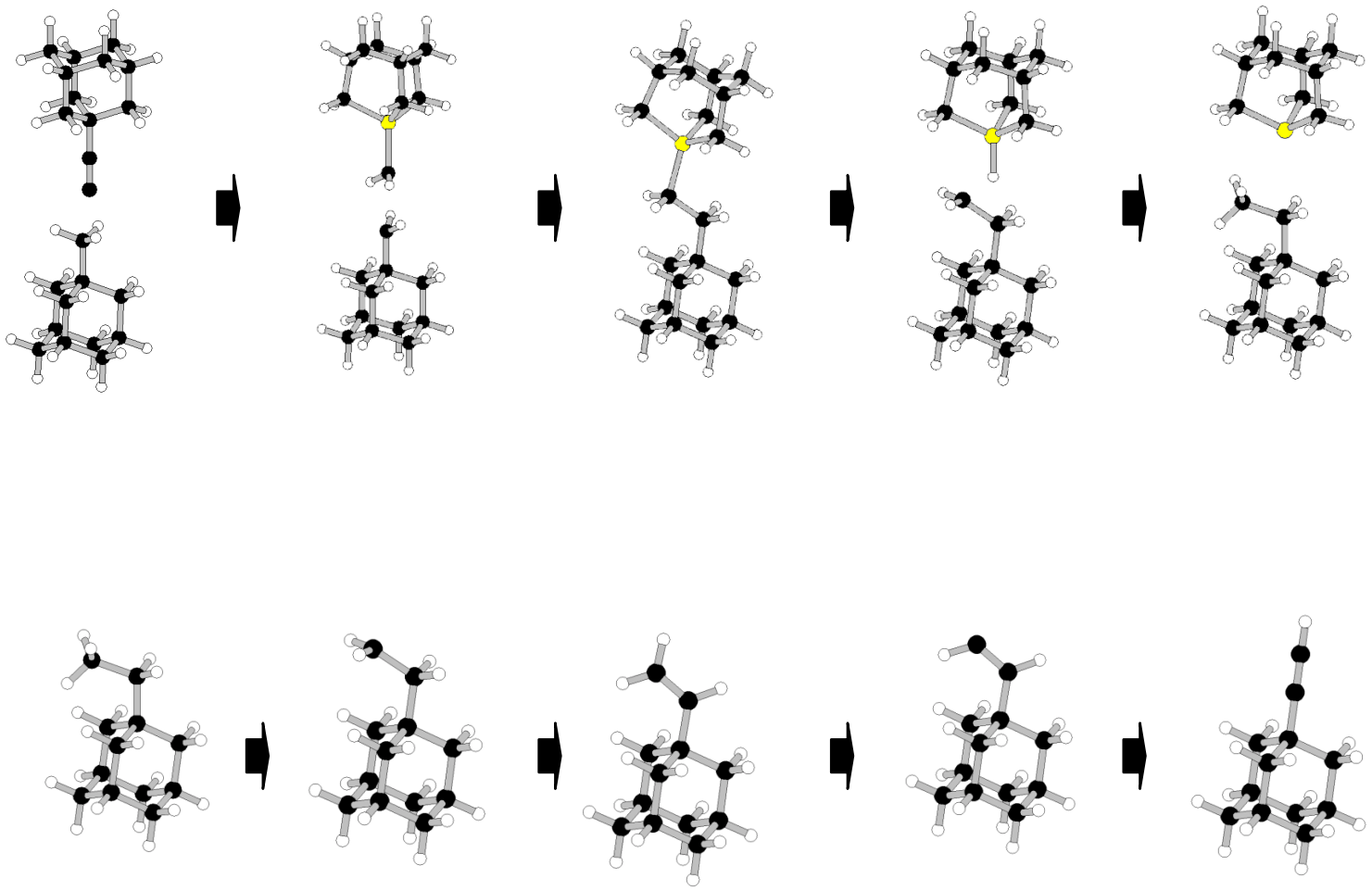
Presentation surfaces



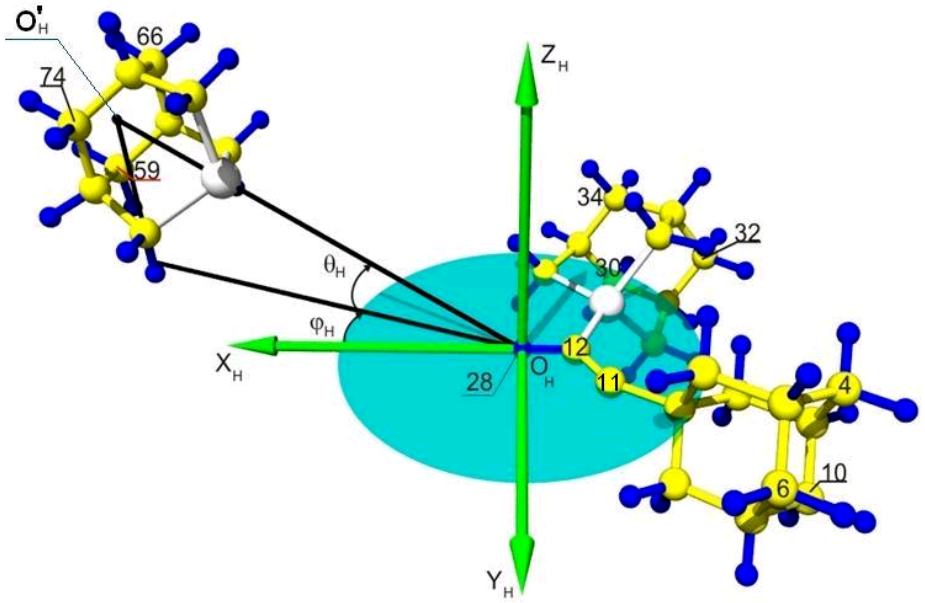
Inputs/outputs

- 9 tools
- 100% process closure
- Can use C_2H_2, Ge_2H_6 as feedstock
- Or use germanium surface for
  C and Ge feedstock presentation
- Six(?) degrees of freedom positional control

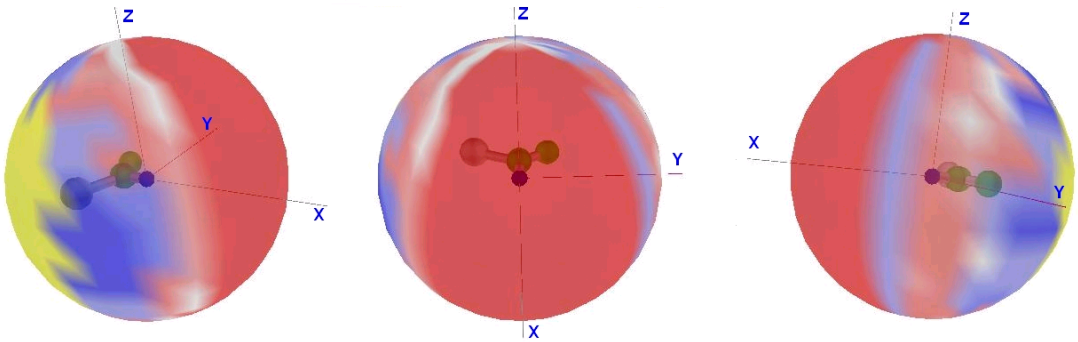
Making HAbst



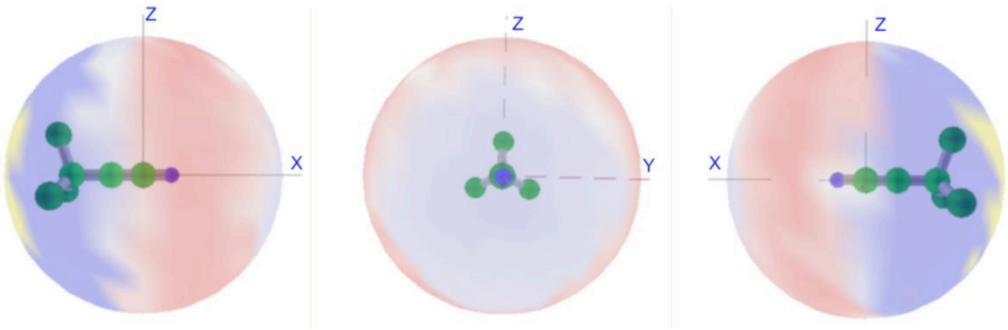
H recharge



H recharge

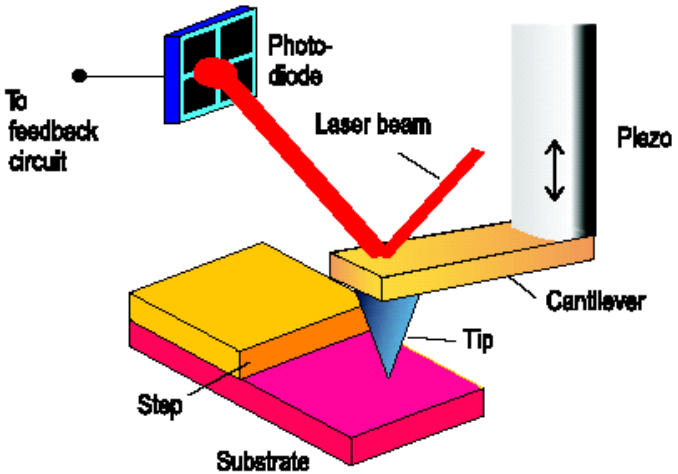


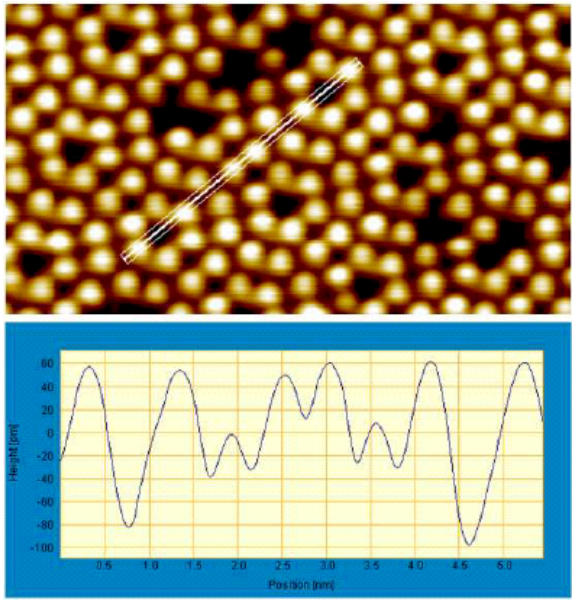
H recharge



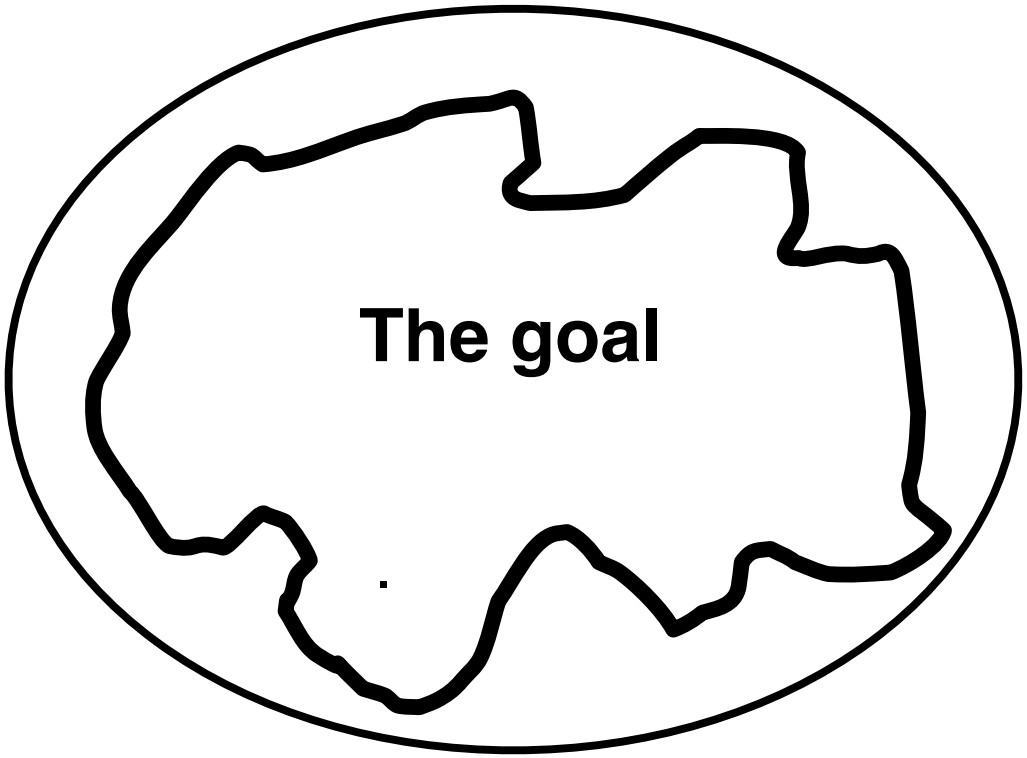
Three views of spherical representation of PES for Reaction I (endoergic = blue, exoergic = red) as a function of tooltip positional angles ϕ and θ (see Fig. 2) expressed on the Cartesian XYZ coordinate system at tooltip separation distance R = 4.85 Å and GeRad rotational angle ρ = +40^{o}. Yellow region is excluded due to handle collision.

Positional assembly



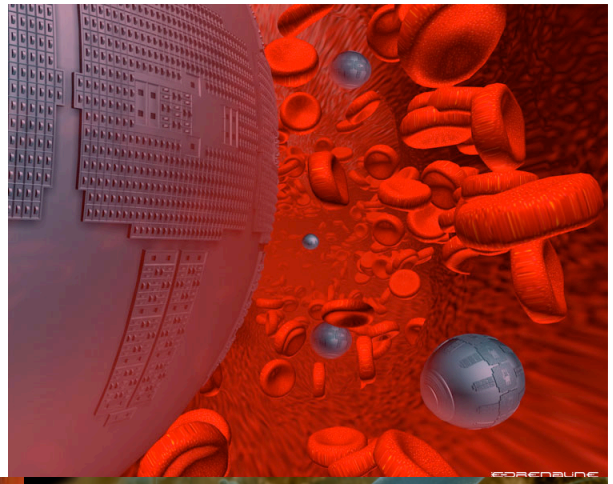


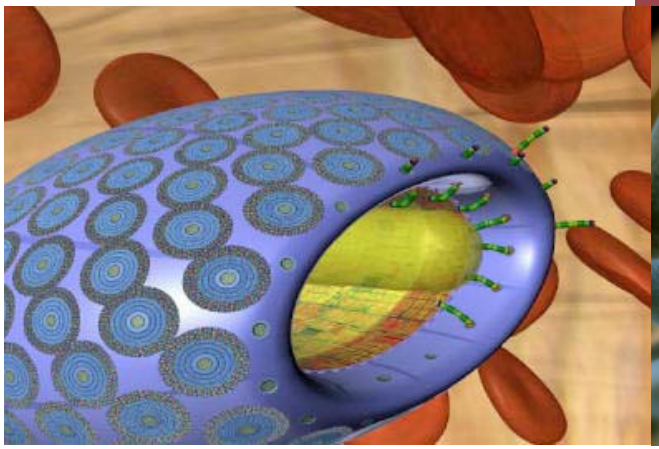
The goal



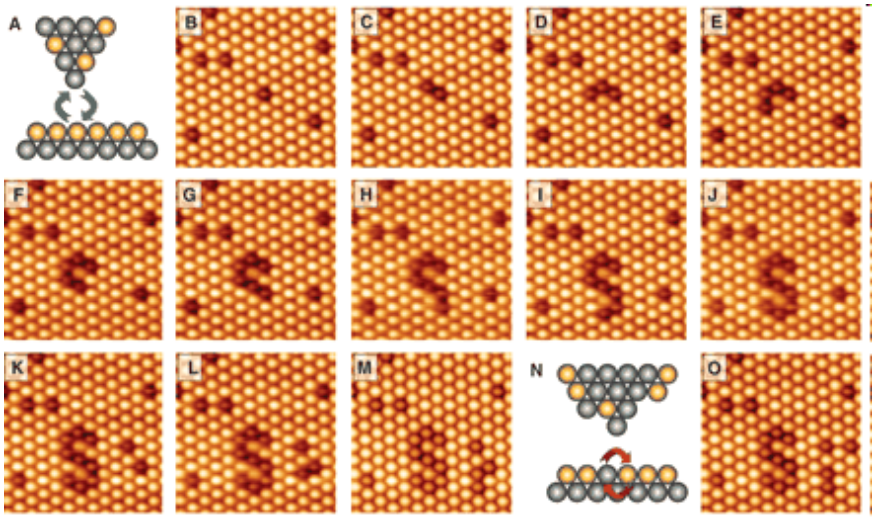
Medicine

- **Respirocytes**
- **Microbivores**
- **Chromallocytes**
- **…**
- ***Designed by Freitas***





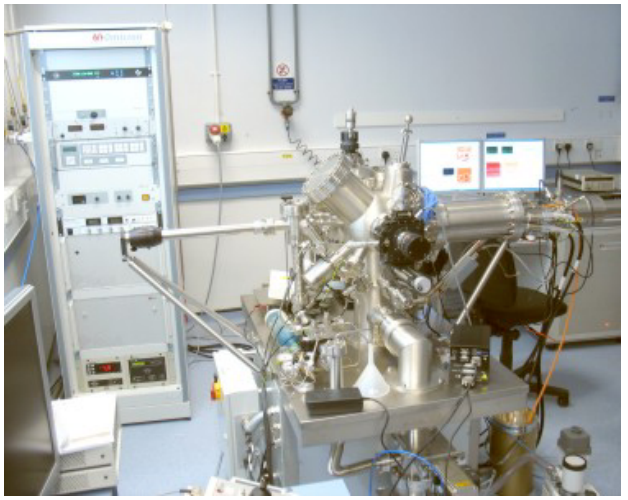
Experimental



"…successive substitution of Sn atoms at the surface one atom at a time with Si atoms coming from the tip."
Science 17 October 2008: vol. 322. no. 5900, pp. 413 – 417. Custance Nanomechanics Group.

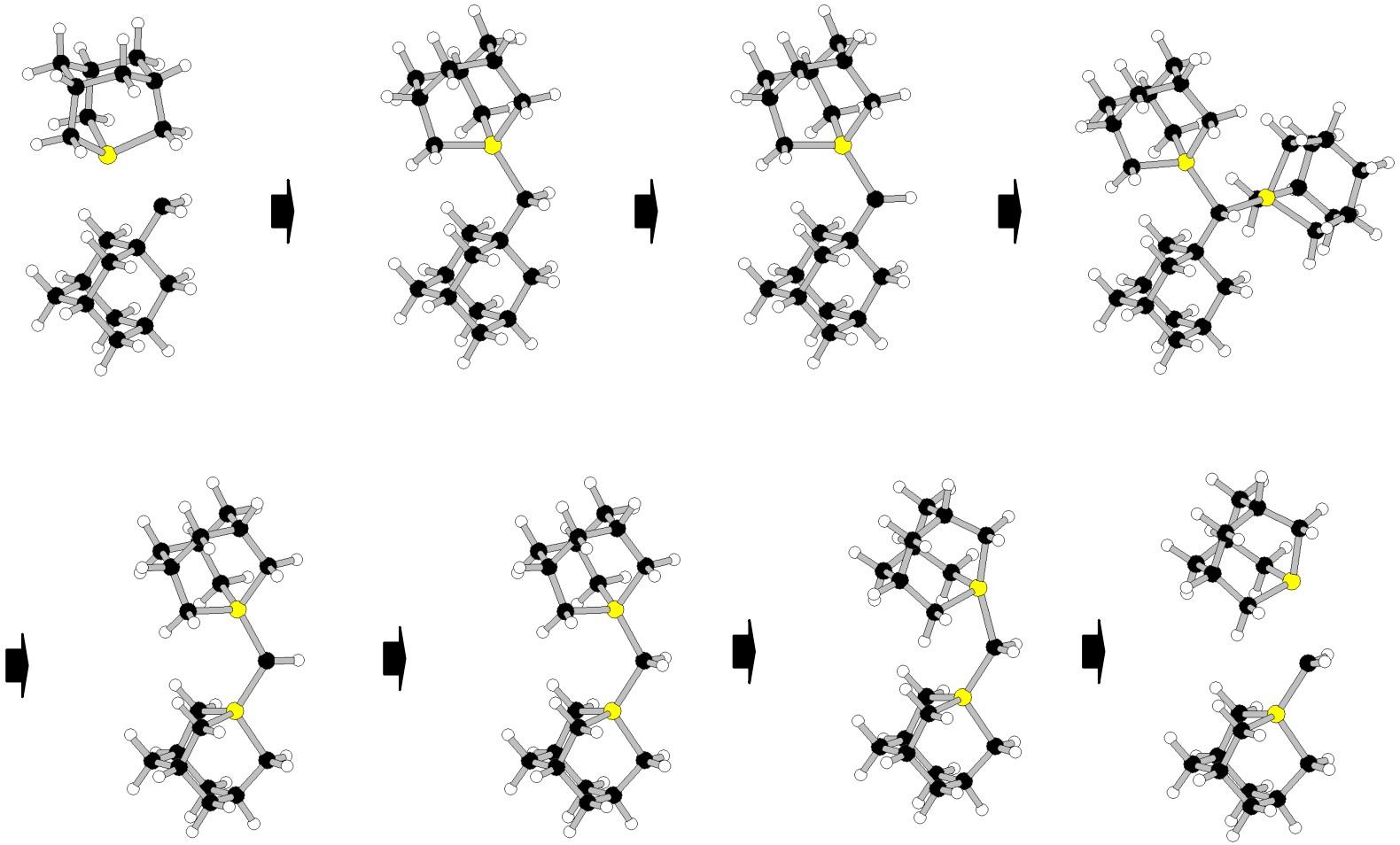
Experimental

- Philip Moriarty, University of Nottingham (U.K.)
- Five-year £1.53M ($3M) grant, August 2008
- Investigate Freitas/Merkle DMS toolset



http://www.MolecularAssembler.com/Nanofactory/Media/PressReleaseAug08.htm

Recharging GM tool



Bearings

Make shaft m-fold symmetric

Make sleeve n-fold symmetric

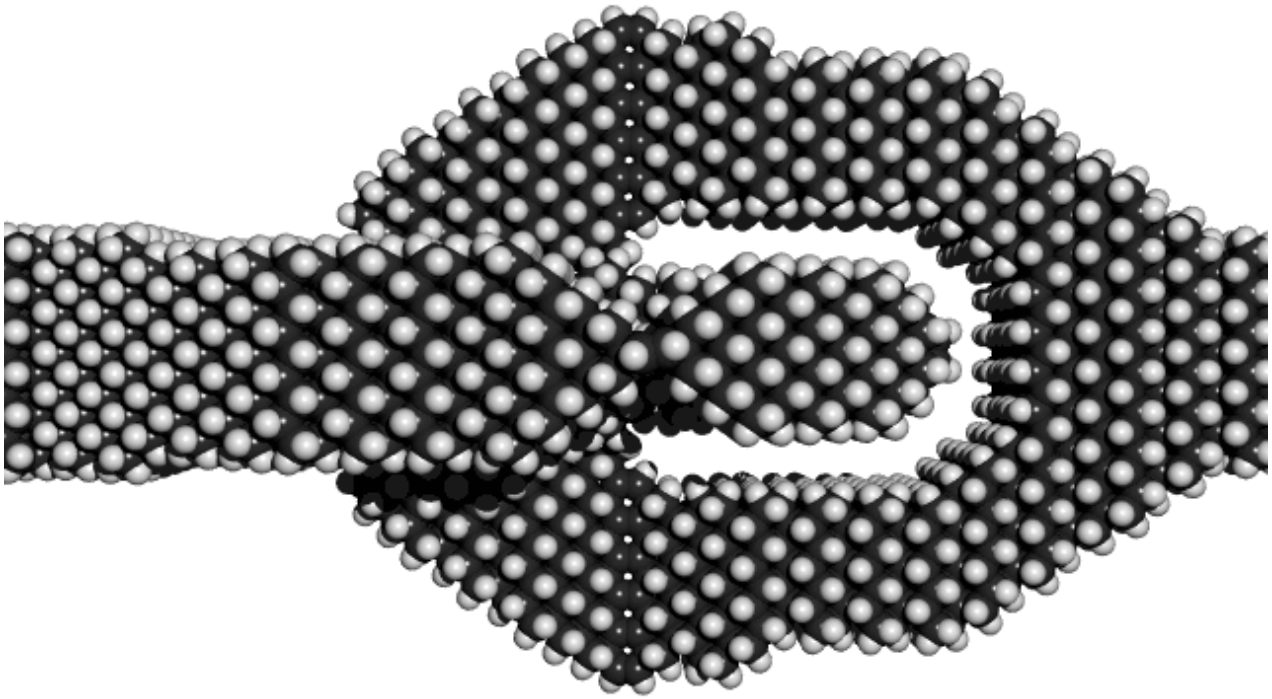
Select m and n so GCD(m,n) is small

- could select m and n relatively prime
- making GCD (m,n) = 1

Period of GCD(m,n)/(m*n)

http://www.zyvex.com/nanotech/bearingProof.html

Hydrocarbon universal joint



High complexity

Over 100 elements in periodic table

Therefore over 100 tools

Combinatorial explosion in considering reaction sequences

Can build almost any structure consistent with physical law

Great flexibility in synthesis

A more specific goal

Hydrocarbon MNT:

The ability to inexpensively manufacture most arrangements of hydrogen and carbon atoms that are consistent with physical law

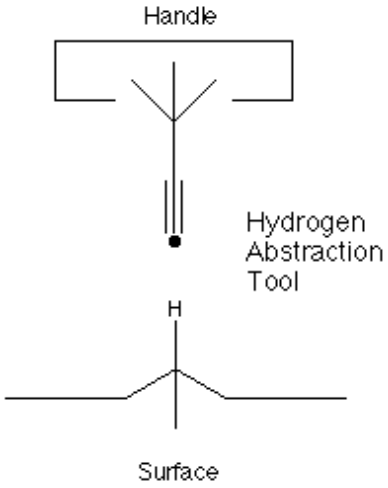
Benefits of Hydrocarbon MNT:

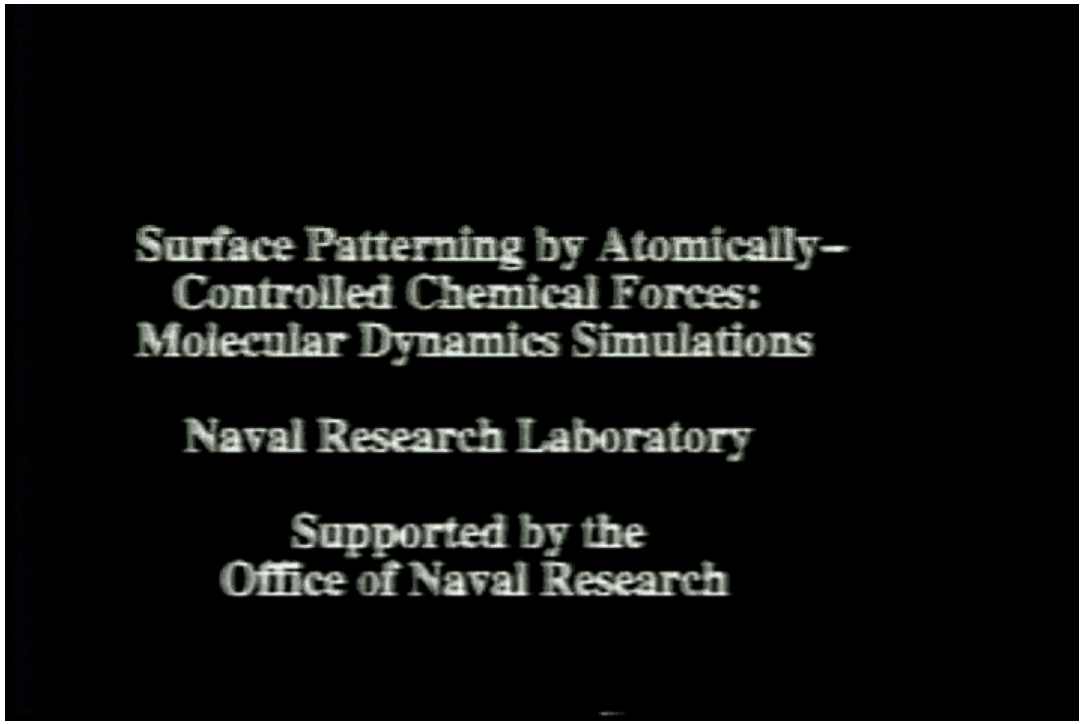
Analysis tractable

Still many highly valuable products

Provides a foothold from which we can clearly achieve the broader goals of MNT

Hydrogen abstraction tool





Computational methods

1630 tooltip/workpiece structures

65 Reaction Sequences

328 reaction steps

354 unique pathological side reactions

1321 reported energies

consuming 102,188 CPU-hours (using 1-GHz CPUs)

Computational methods

Gaussian 98

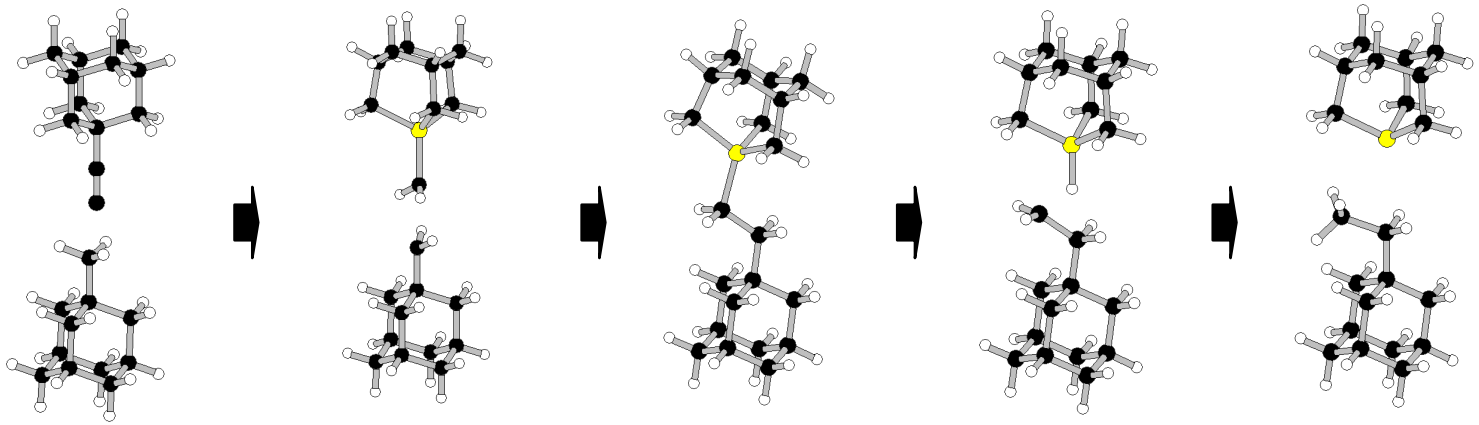
Singlet or doublet geometries optimized with no constrained degrees of freedom using spin-unrestricted Hartree-Fock (UHF) analysis at the B3LYP/3-21G* level of theory

Single point energy calculations performed at the B3LYP/6-311 +G(2d,p) level of theory

The mean absolute deviation from experiment (MAD) for B3LYP/ 6-311+G(2d,p) // B3LYP/3-21G* energies is estimated as 0.14 eV for carbon-rich molecules

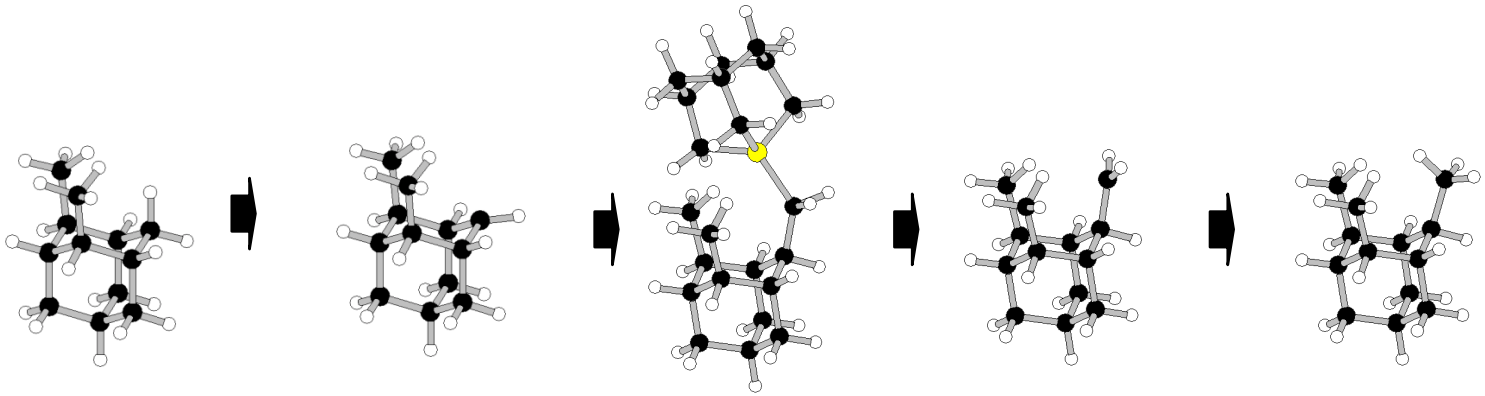
Barriers of 0.4 eV against side reactions in most cases

C placement



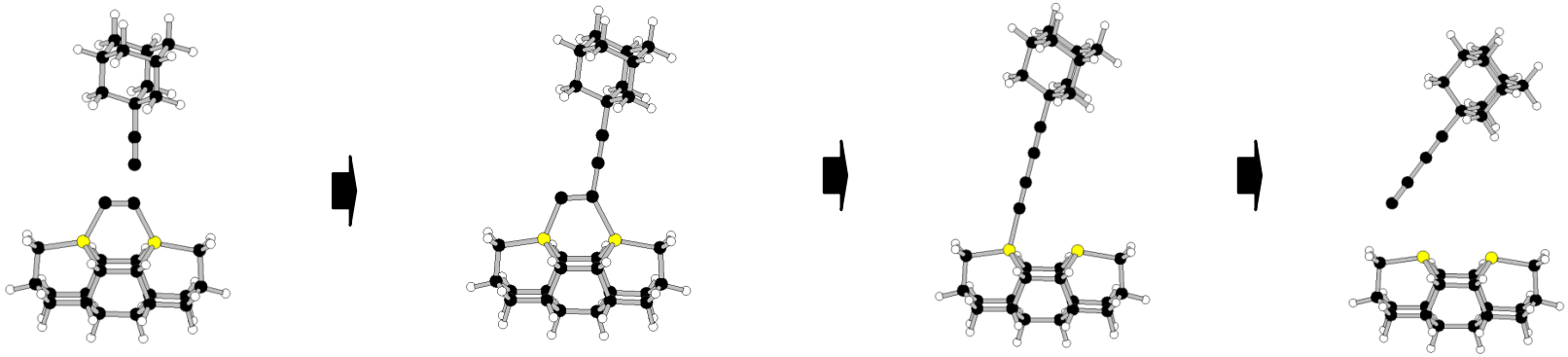
2nd C placement on C on C(111)
C radical addition to C radical -3.12 eV
(note undesired H abstraction by C radical from C radical, +0.69 eV barrier)
GeRad removal +2.74 eV (note Ge-C bond is “soft”)
HDon hydrogenate C radical -0.65 eV

C placement

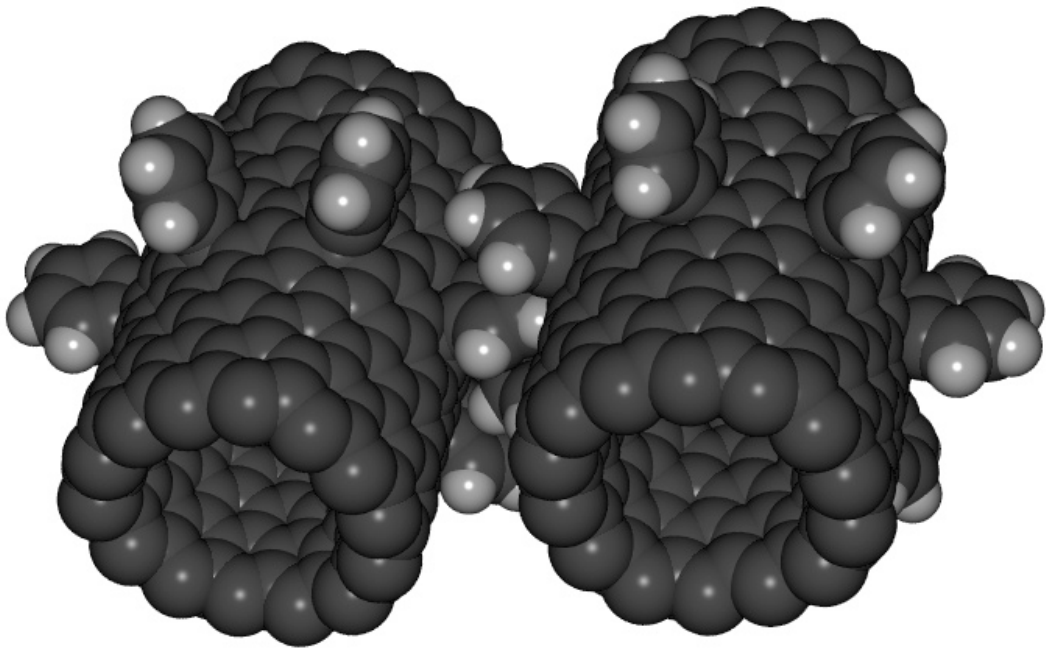


3rd C placement on adjacent site of C(111) surface

Making polyyne chain

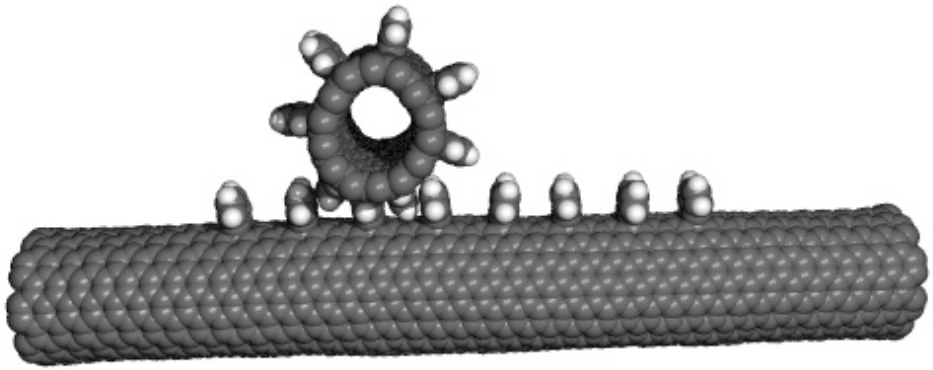


Bucky gears



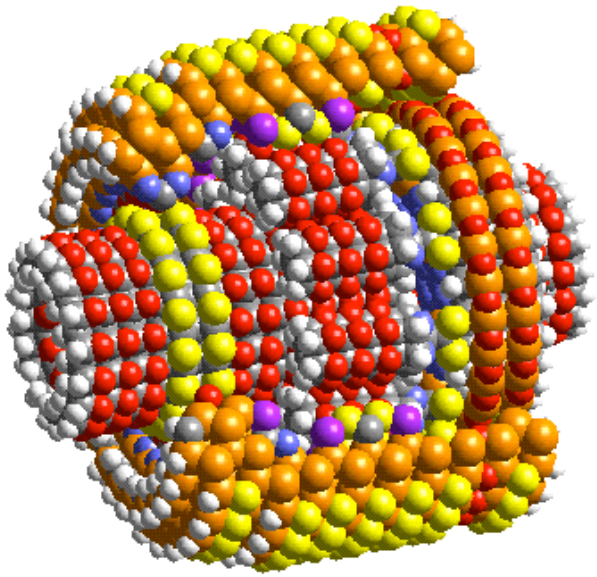
NASA Ames

Rotary to linear

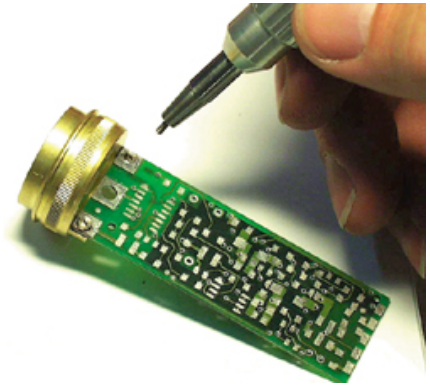


NASA Ames

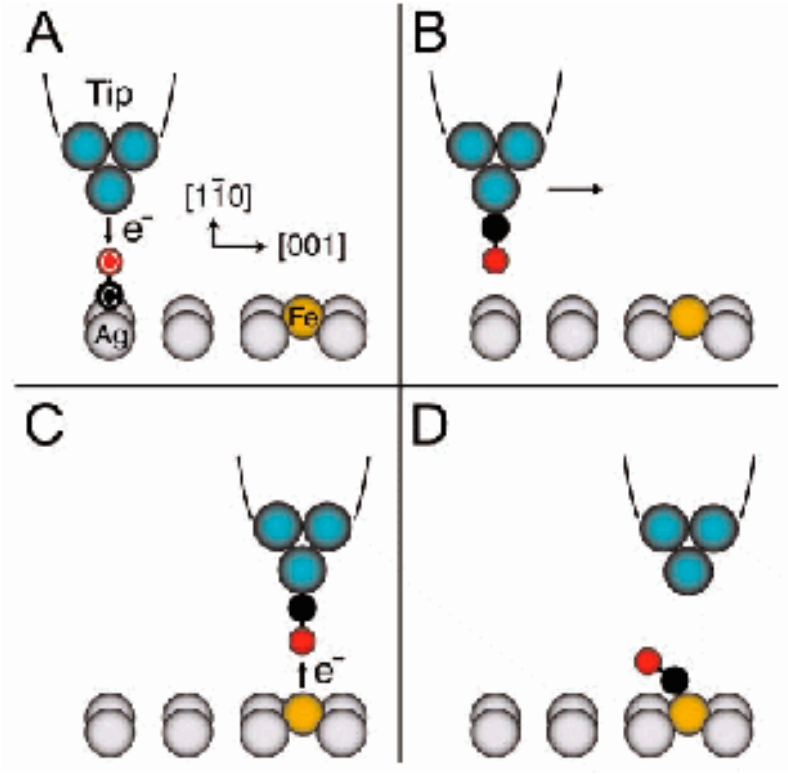
Planetary gear



Positional assembly

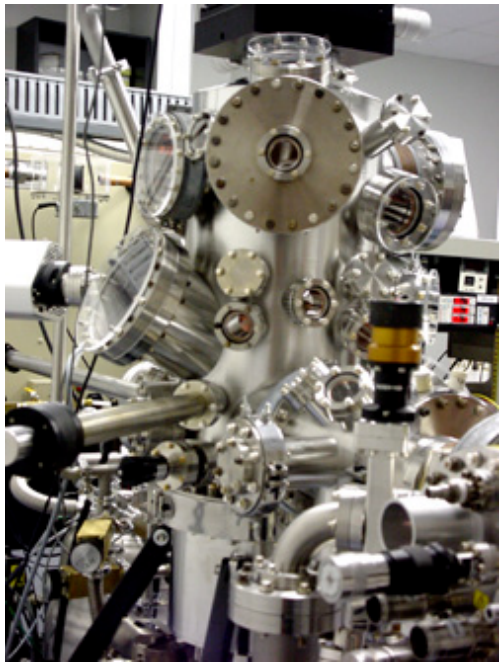


Experimental



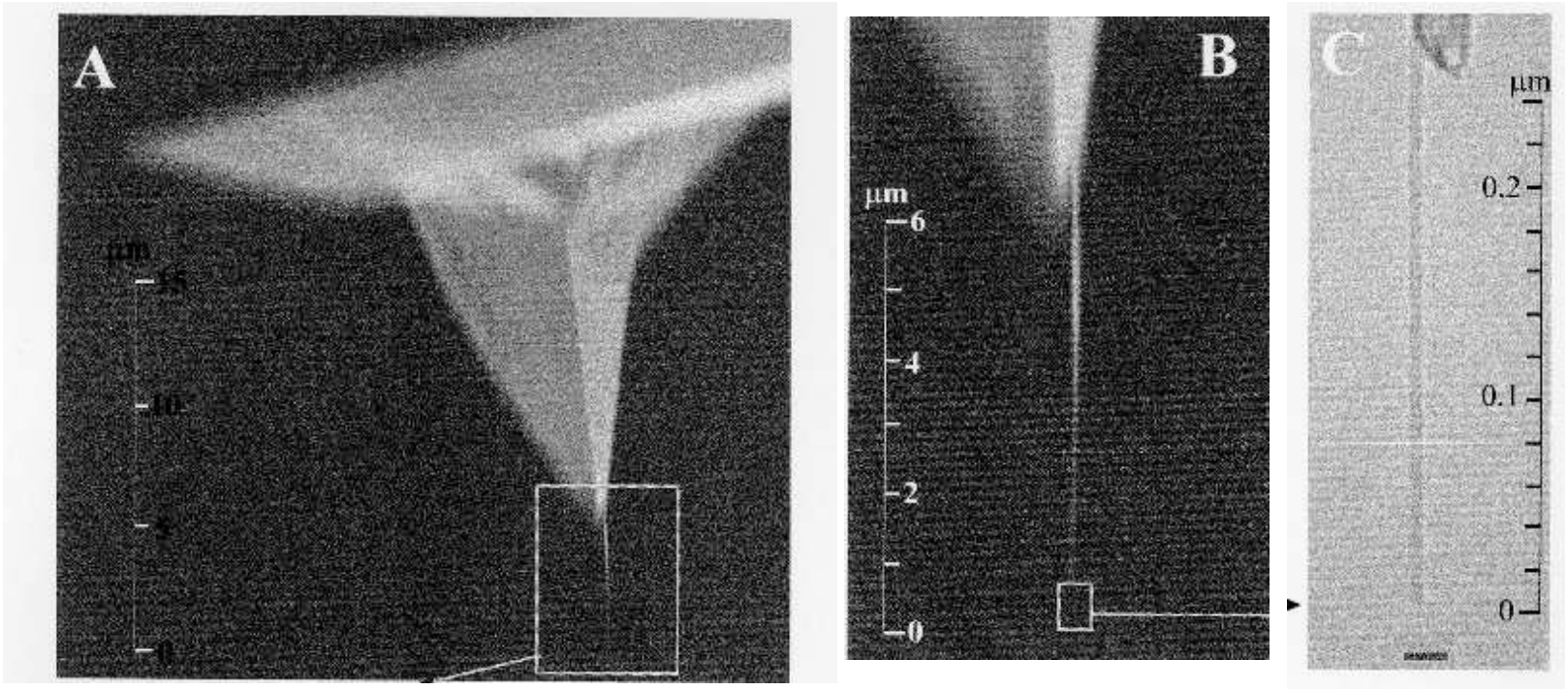
H. J. Lee and W. Ho, SCIENCE **286,** p. 1719, NOVEMBER 1999

Experimental



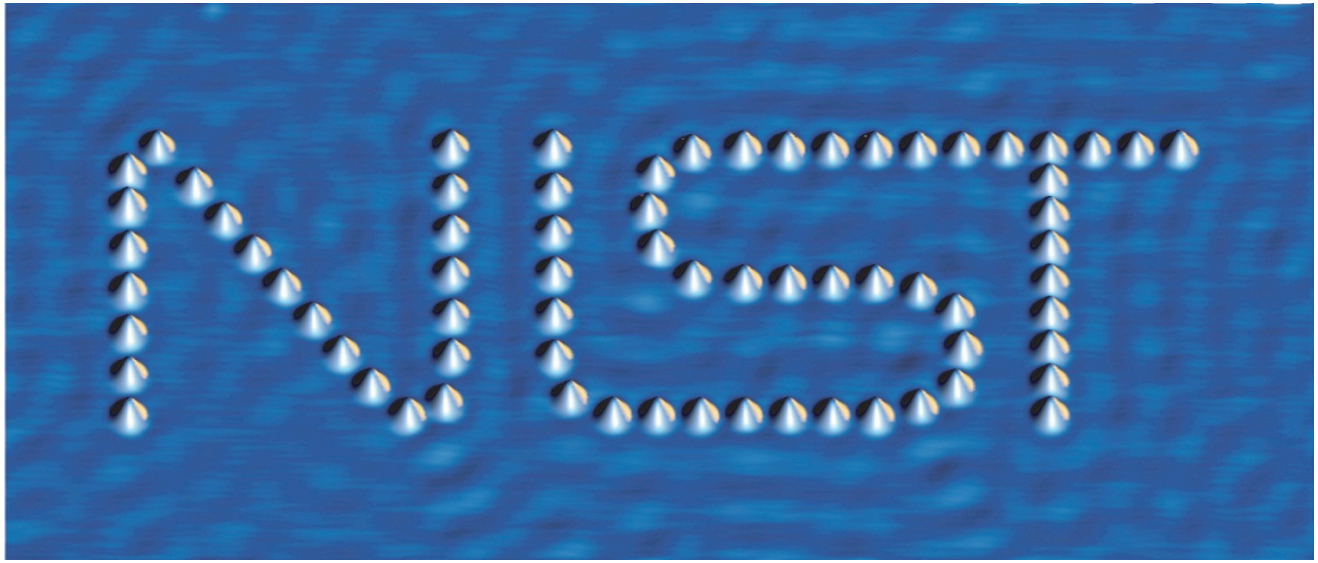
SPM at Zyvex

Bucky tube glued to SPM tip



Hongjie Dai et al. Nature 384, 147-151 (1996)

Experimental



A 40-nanometer-wide NIST logo made with cobalt atoms on a copper surface

Controlling the Dynamics of a Single Atom in Lateral Atom Manipulation
Joseph A. Stroscio and Robert J. Celotta, Science, Vol 306, Issue 5694, 242-247, 8 October 2004
http://www.nist.gov/public_affairs/releases/hiphopatoms.htm

Experimental

Molecule Cascades

A. J. Heinrich,*† C. P. Lutz,* J. A. Gupta, D. M. Eigler

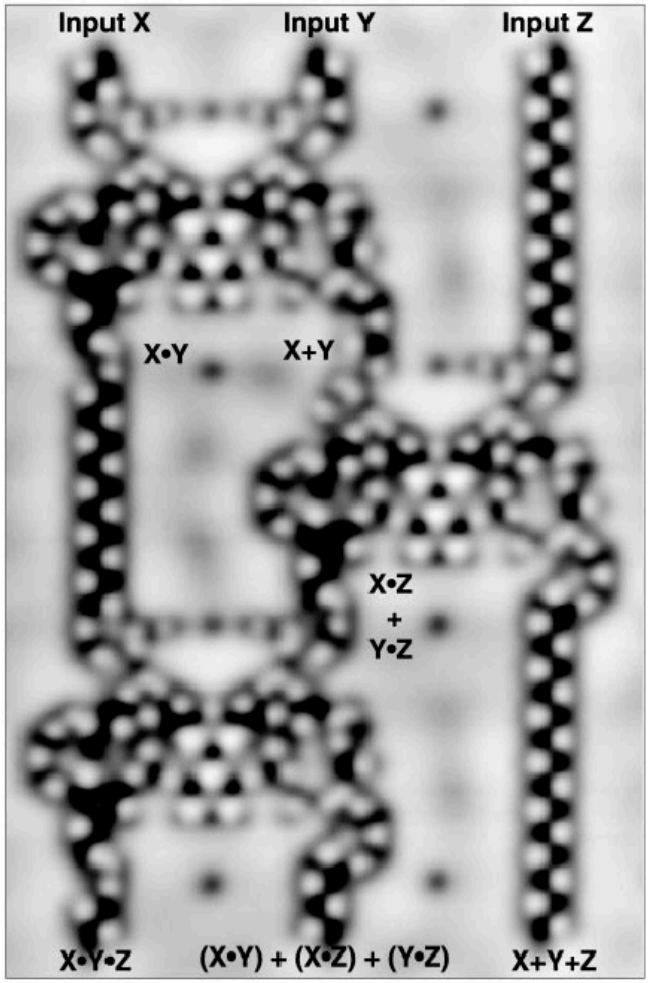
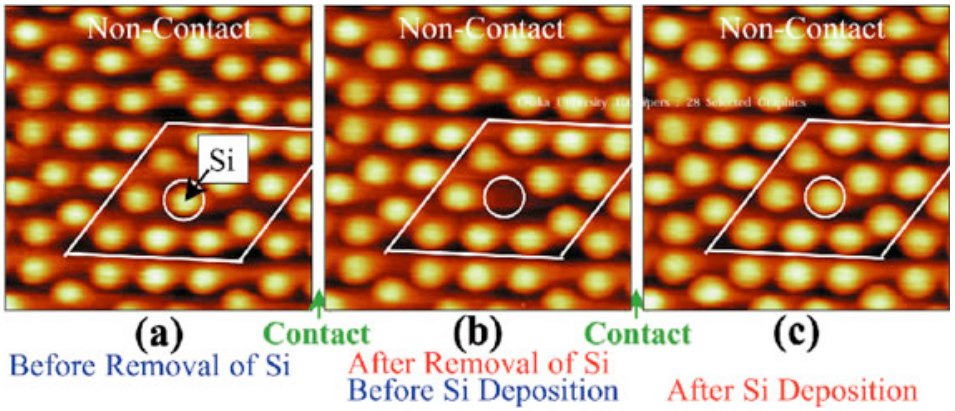


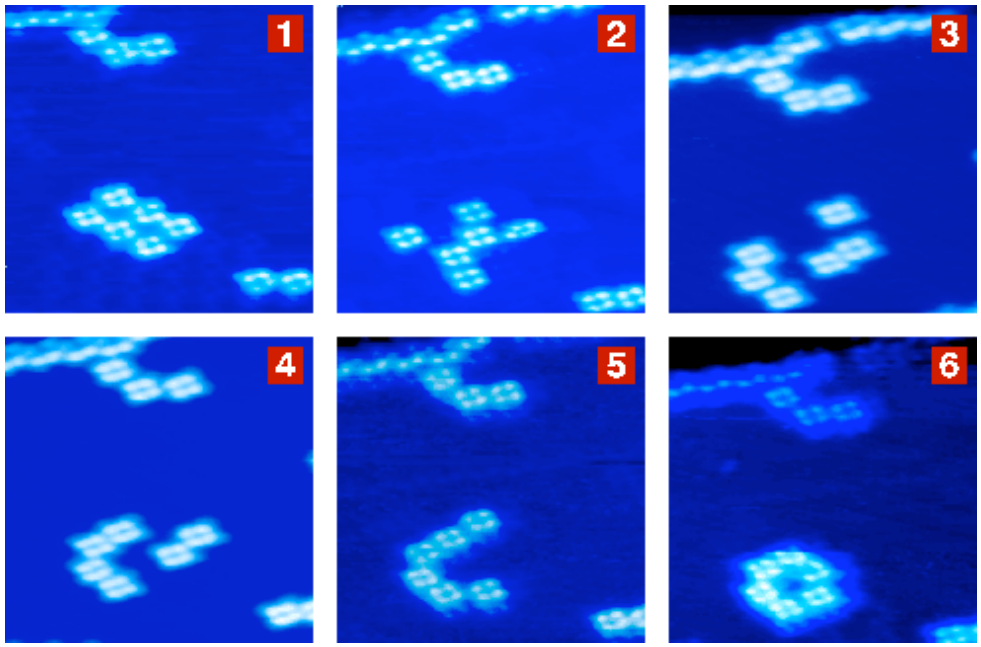
Fig. 9. STM image (12 nm by 17 nm) of a three-input sorter in the initial setup (I = 40 pA; V = 10 mV). The symbol + denotes logic OR, and • denotes logic AND. Images with one or more inputs triggered are not shown.

Experimental



Mechanical vertical manipulation of selected single atoms by soft nanoindentation using near contact atomic force microscopy, Noriaki Oyabu, Oscar Custance, Insook Yi, Yasuhiro Sugawara, Seizo Morita1, *Phys. Rev. Lett.* 90(2 May 2003):176102.

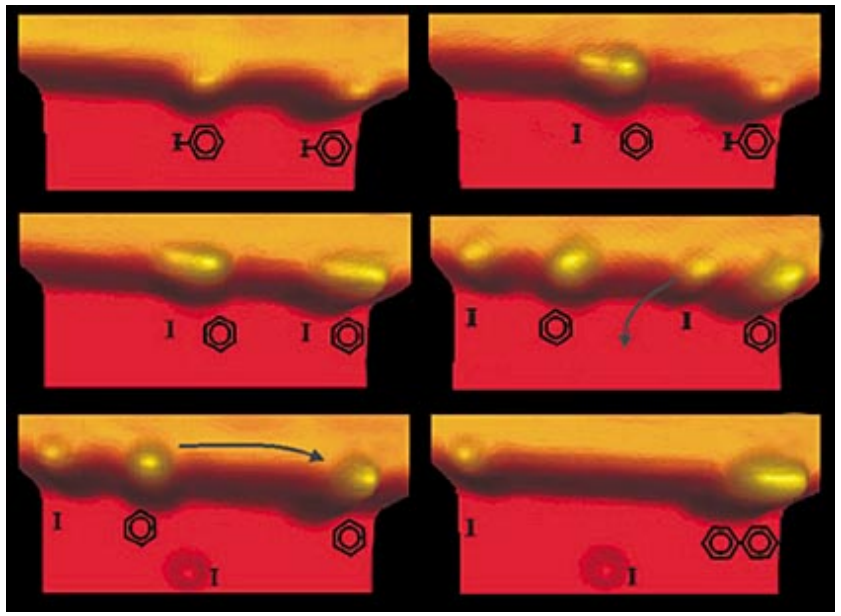
Experimental work



Gimzewski et al.

Experimental

STM images show two iodobenzene molecules on a Cu substrate (top left). Next, a voltage pulse from the STM tip breaks the iodine-phenyl bonds (top right and middle left). The iodine atom is moved out of the way (middle right), and finally, the two phenyls are brought together (bottom). C&EN News 10/2/00



Manipulation and bond formation by STM at 20 K

Saw-Wai Hla et al., Physical Review Letters 85, 2777-2780, September 25 2000 http://www.phy.ohiou.edu/~hla/7.pdf

Invited Review
Engineering of single molecules with a scanning tunneling microscope tip

SAW-WAI HLA and KARL-HEINZ RIEDER

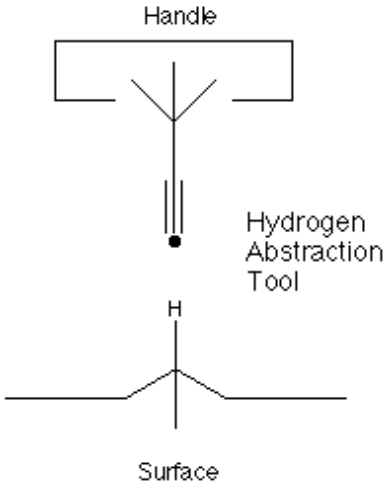
Superlattices and Microstructures, Vol. 31, No. 1, 2002
http://www.phy.ohiou.edu/~hla/20.pdf
Also see http://www.phy.ohiou.edu/~hla/publication.html

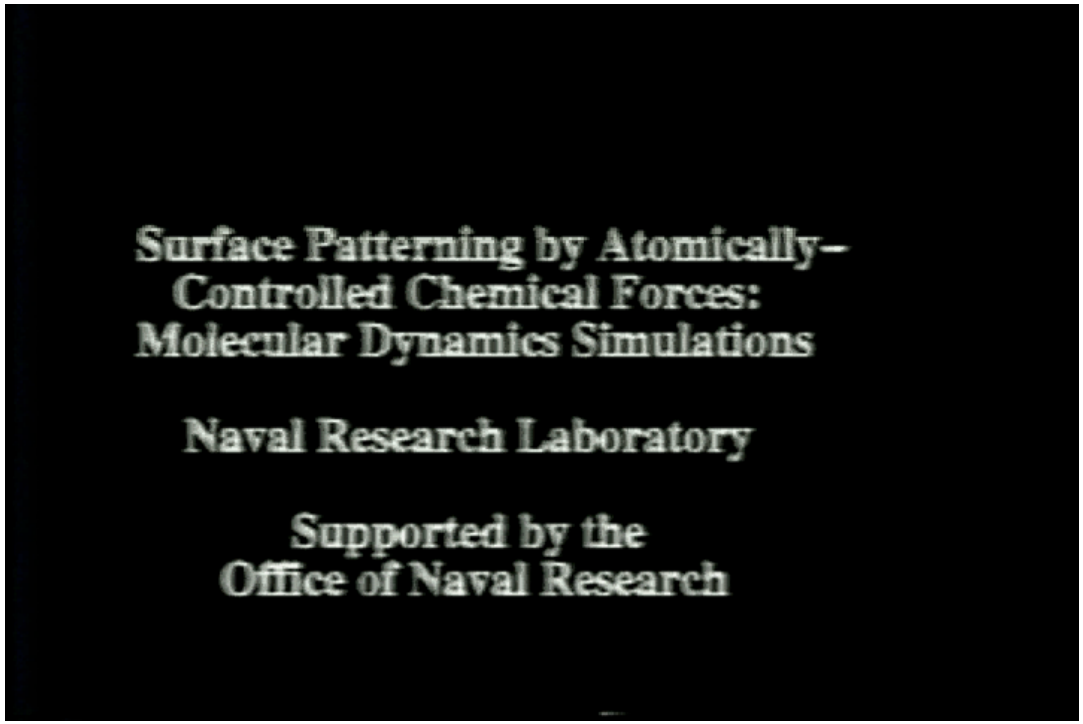
Arranging atoms

"...a long time chemist's dream of construction of individual molecules from the basic building blocks has now become a reality."

Superlattices and Microstructures, Vol. 31, No. 1, 2002
http://www.phy.ohiou.edu/~hla/20.pdf

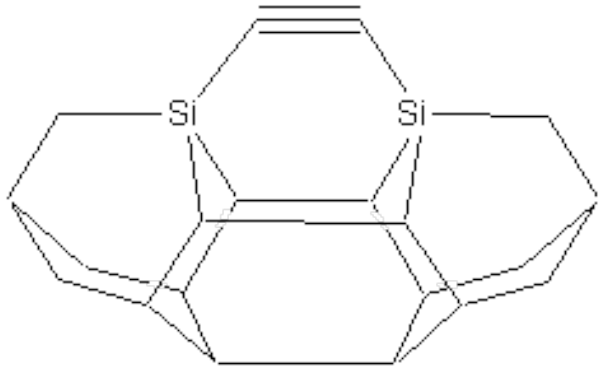
Theoretical H abstraction





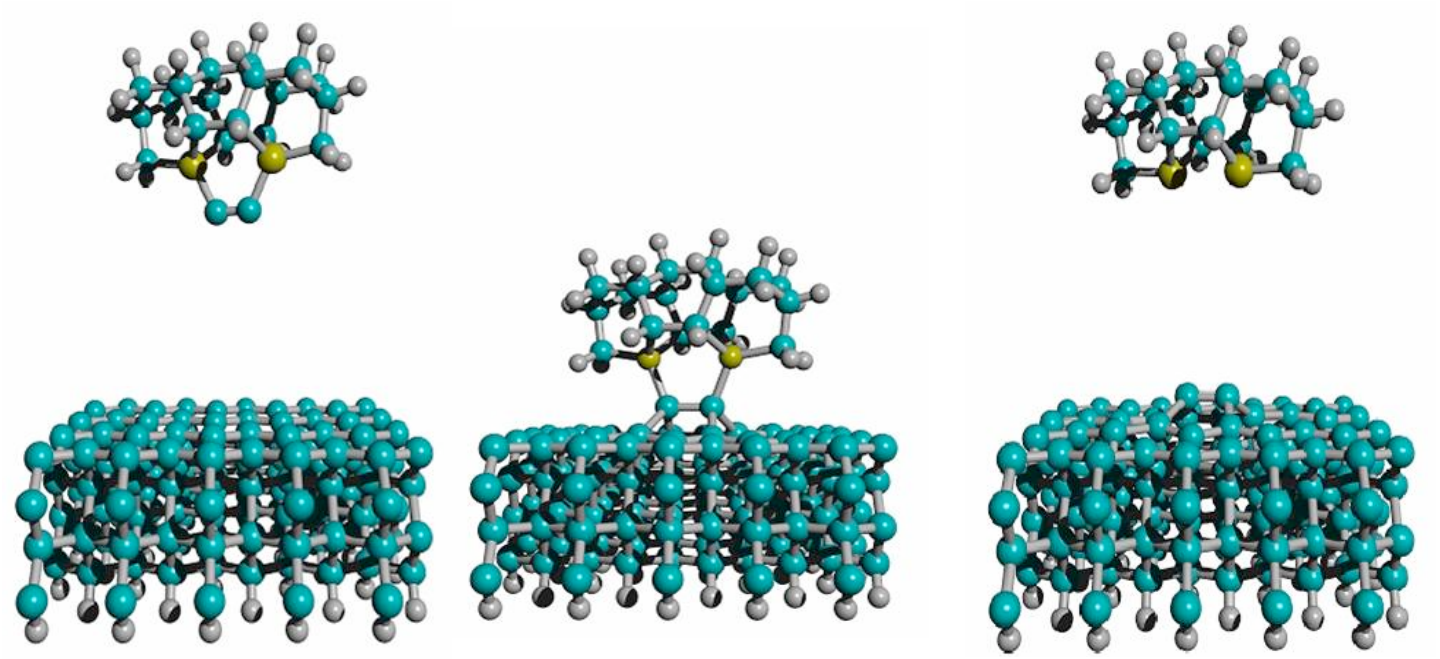
See *High-level Ab Initio studies of hydrogen abstraction from prototype hydrocarbon systems* by Berhane Temelso et al.

Adding carbon



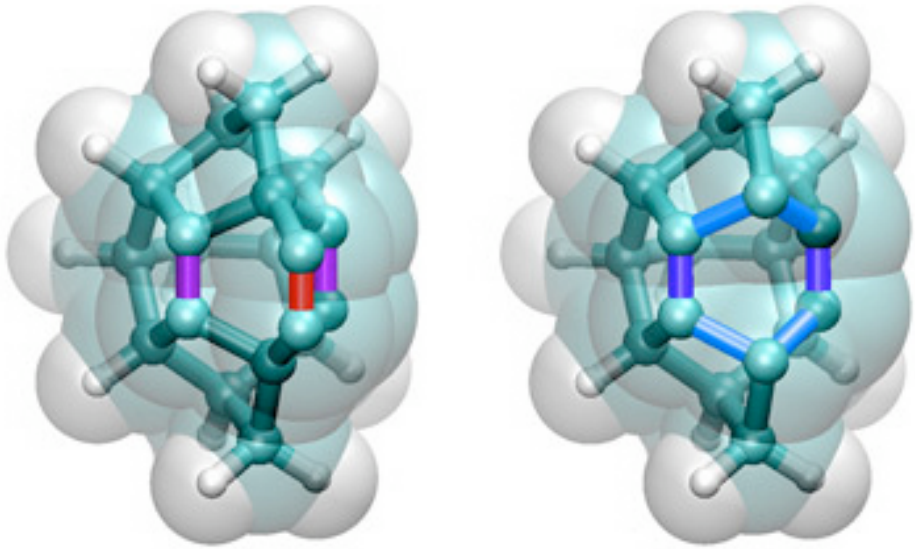
Theoretical Analysis of a Carbon-Carbon Dimer Placement Tool for Diamond Mechanosynthesis
by Ralph C. Merkle, Robert A. Freitas Jr. *J. Nanosci. Nanotechnol.* 3(August 2003):319-324.

Adding carbon



Theoretical Analysis of Diamond Mechanosynthesis. Part II. C2 Mediated Growth of Diamond C(110) Surface via Si/Ge-Triadamantane Dimer Placement Tools, J. Comp. Theor. Nanosci. 1(March 2004). David J. Mann, Jingping Peng, Robert A. Freitas Jr., Ralph C. Merkle, In press.

Adding carbon



Allis D.G. and Drexler K.E. "Design and Analysis of a Molecular Tool-Tip for Carbon Transfer in Mechanosynthesis." Journal of Computational and Theoretical Nanotechnology, *in press*

Theoretical

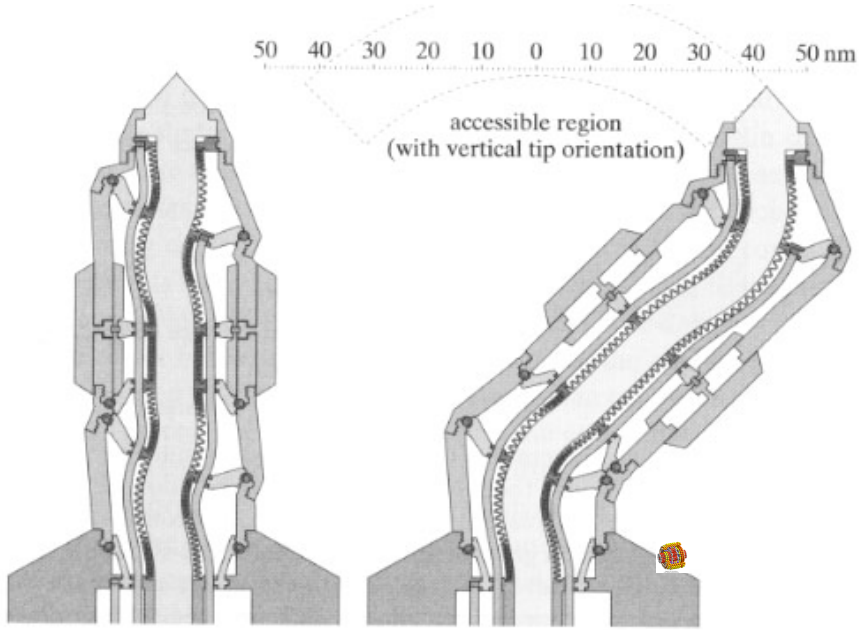


Figure 13.14. Cross section of a stiff manipulator arm, showing its range of motion (schematic).

Thermal noise

Assume a linear restoring force k such that

$F_{restore} = k\,x$

$E = \frac{1}{2}\,k\,x^2$

(SI units for the restoring force are N/m)

Maxwell-Boltzmann distribution

$$\frac{\exp(\frac{-E}{k_b T})}{\int_{-\text{inf}}^{+\text{inf}} \exp(\frac{-E}{k_b T})} \qquad \frac{\exp(\frac{-kx^2}{2k_b T})}{\int_{-\text{inf}}^{+\text{inf}} \exp(\frac{-kx^2}{2k_b T})} \qquad \frac{\exp(\frac{-x^2}{2\sigma})}{\int_{-\text{inf}}^{+\text{inf}} \exp(\frac{-x^2}{2\sigma})}$$

σ: mean positional error

k: restoring force

k_b: Boltzmann's constant

T: temperature

Thermal noise

$$\sigma^2 = \frac{k_b T}{k}$$

σ: mean positional error

k: restoring force

k_b: Boltzmann's constant

T: temperature

Thermal noise

$$\sigma^2 = \frac{k_b T}{k}$$

σ: 0.02 nm (0.2 Å)

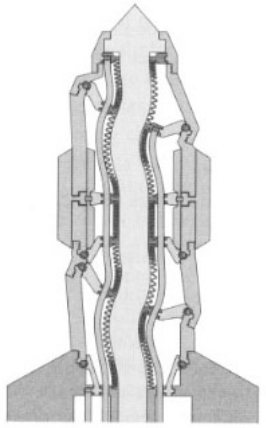
k: 10 N/m

k_b: 1.38×10^{-23} J/K

T: 300 K

Stiffness

$$k = \frac{3\pi r^4 E}{4L^3}$$



E: Young's modulus

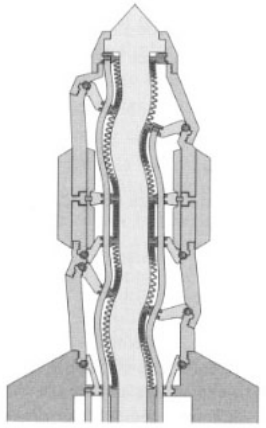
k: transverse stiffness

r: radius

L: length

Stiffness

$$k = \frac{3\pi r^4 E}{4L^3}$$



E: 10^{12} N/m^2

k: 10 N/m

r: 8 nm

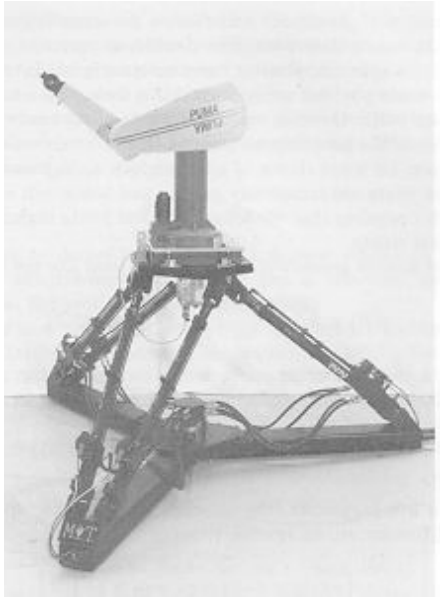
L: 100 nm

Stewart platform

Stewart platform

References:

http://www.igd.fhg.de/www/igd-a4/research/motion_base/letsmove.html



Stewart platform

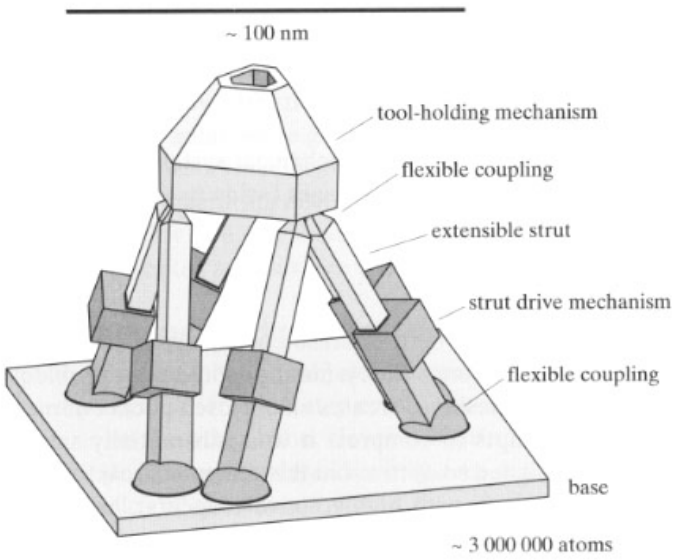
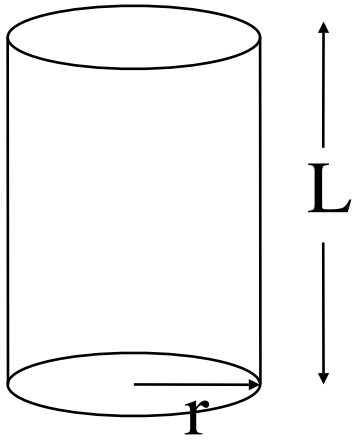


Figure 16.4. A positioning mechanism based on the Stewart platform (schematic). Each strut has a joint at each end, shown for simplicity as ball-and-socket joints at the base and as flexible point attachments at the top. Each strut has a set of actuators able to adjust its length. See Figure 16.5.

Stiffness

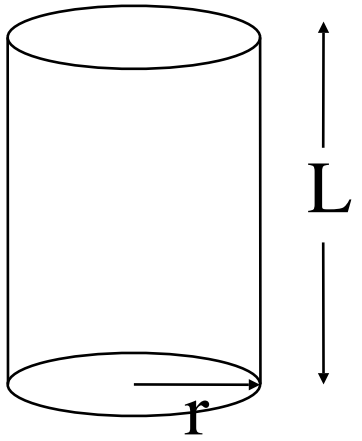
$$k = \frac{\pi r^2 E}{L}$$



E: Young's modulus
k: longitudinal stiffness
r: radius
L: length

Stiffness

$$k = \frac{\pi r^2 E}{L}$$



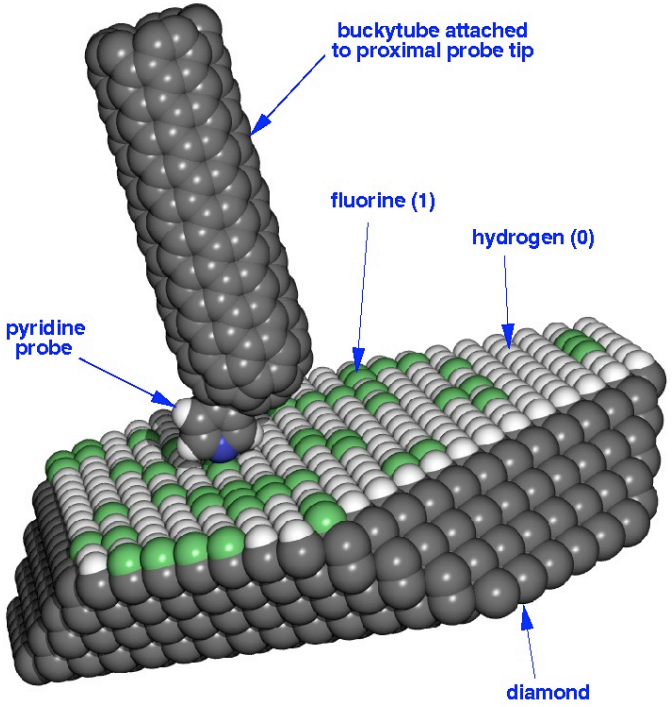
E: 10^{12} N/m^2

k: 500 N/m

r: 4 nm

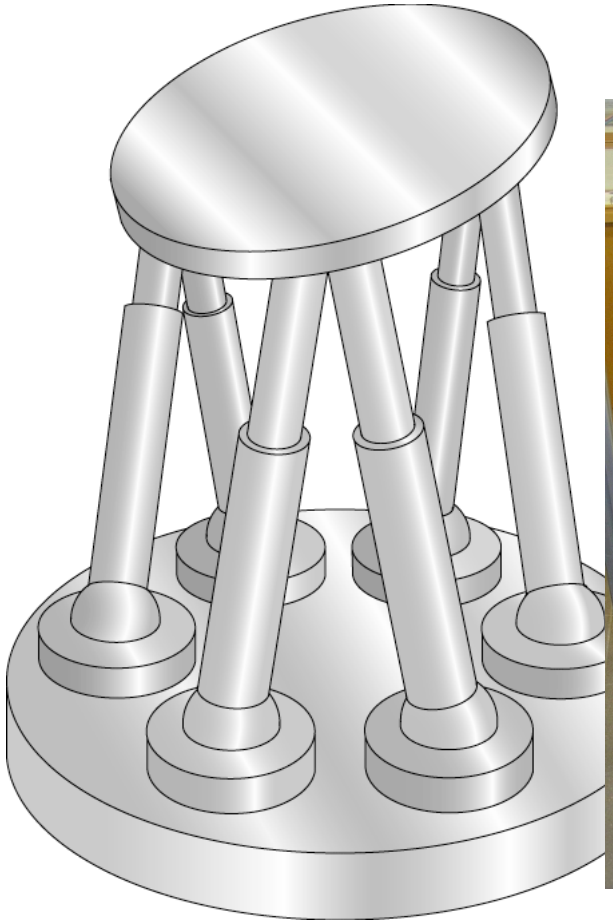
L: 100 nm

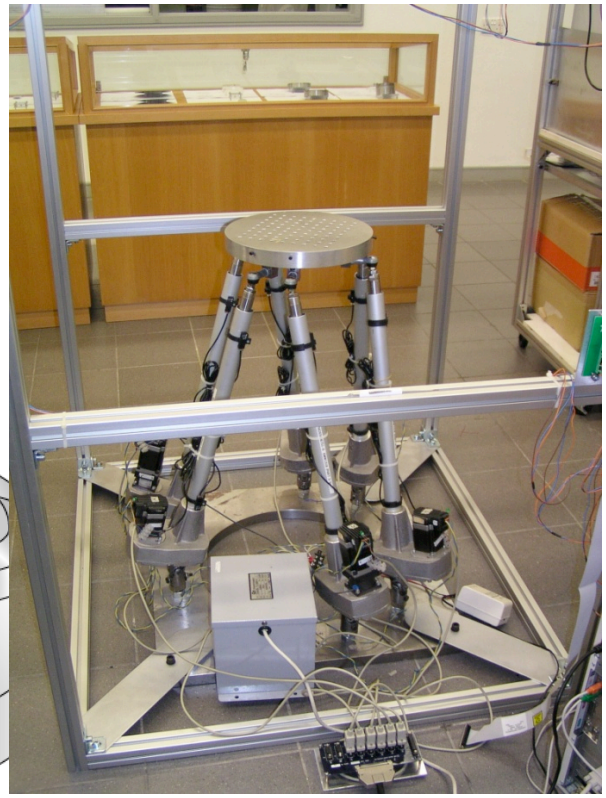
High density memory (theoretical)

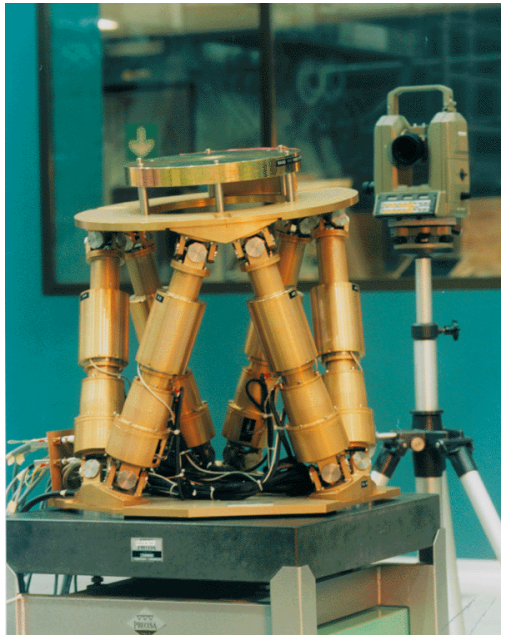


End of Slides

Stewart platform

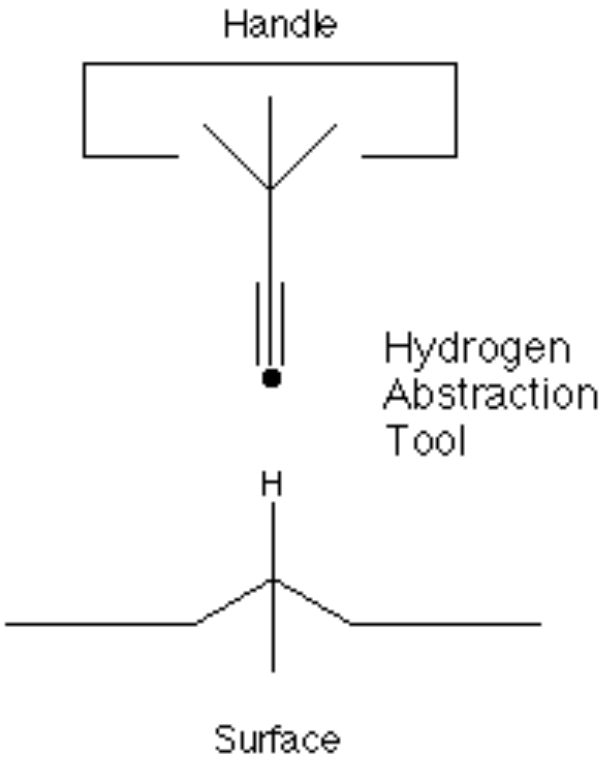




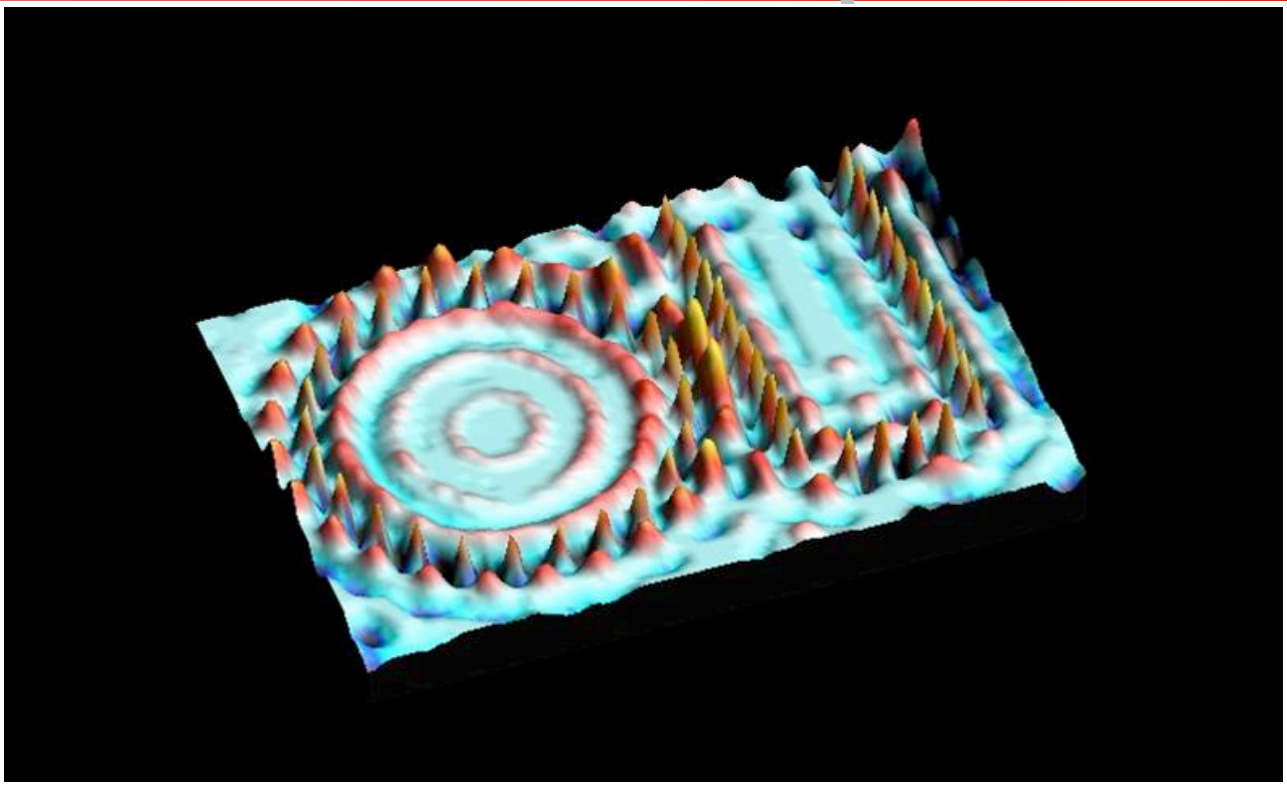


Stewart platform

Hydrogen abstraction tool



Experimental



The Ohio University atomic logo is written on a Ag (111) surface at 6 K temperature. (51 silver atoms, 42 nm x 26 nm area.
Image from Saw-Wai Hla lab)

Making diamond today

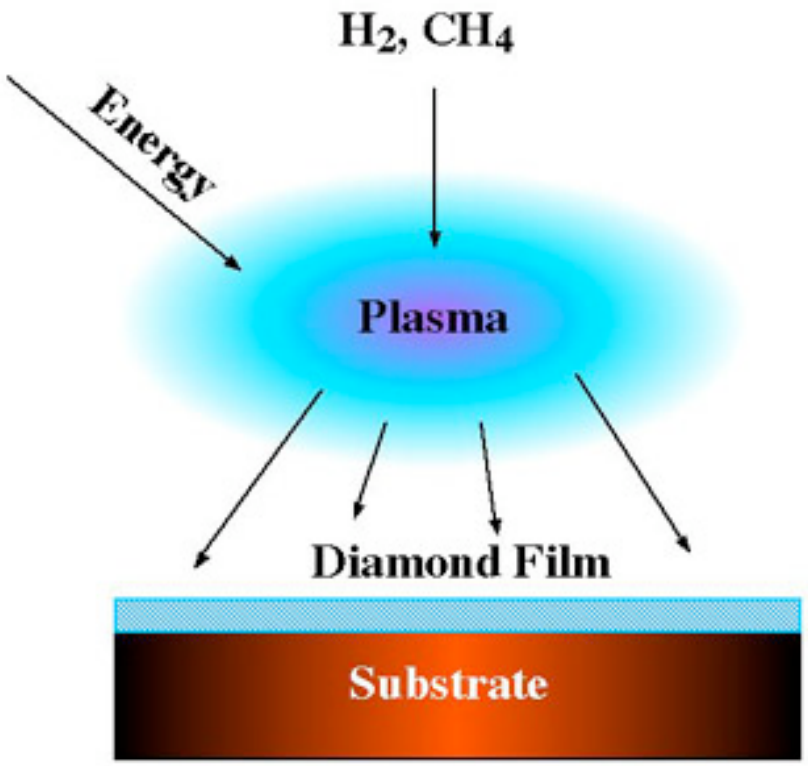
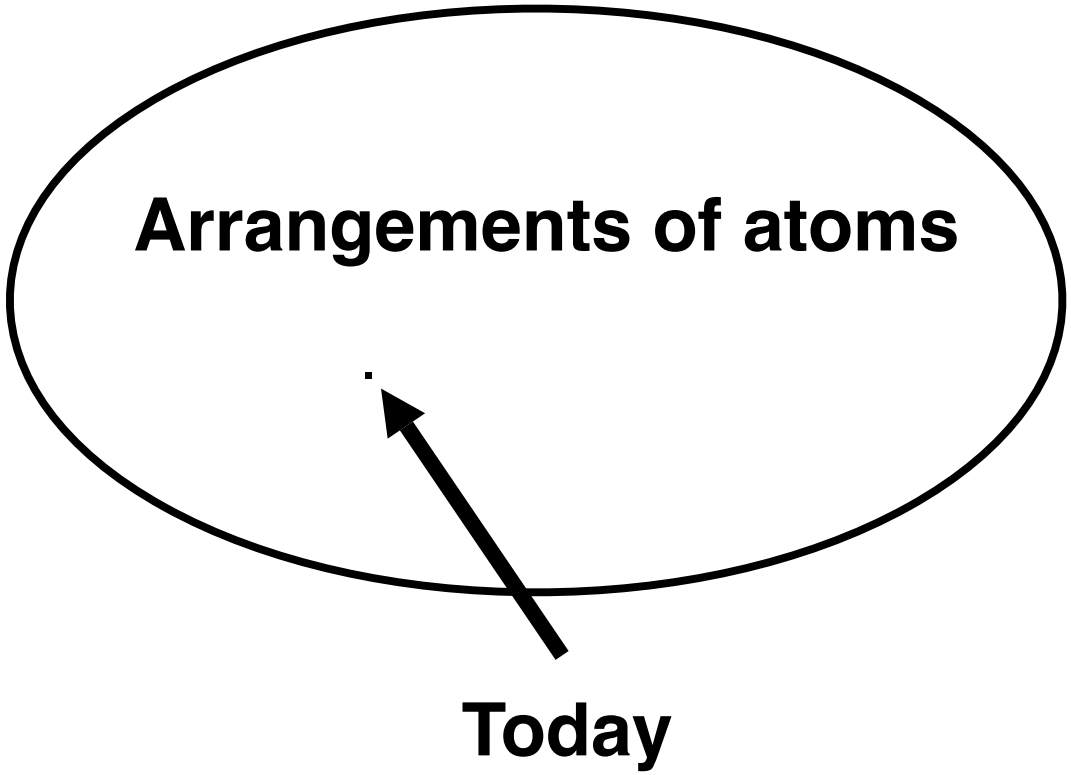
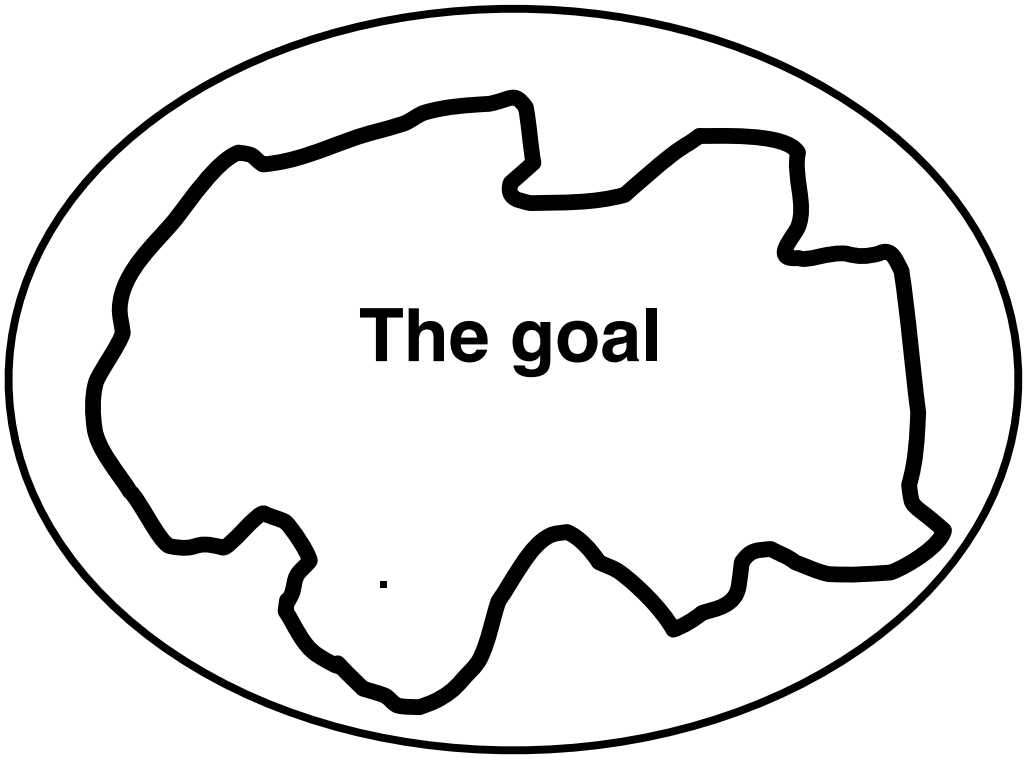


Illustration courtesy of P1 Diamond Inc.

The goal



The goal



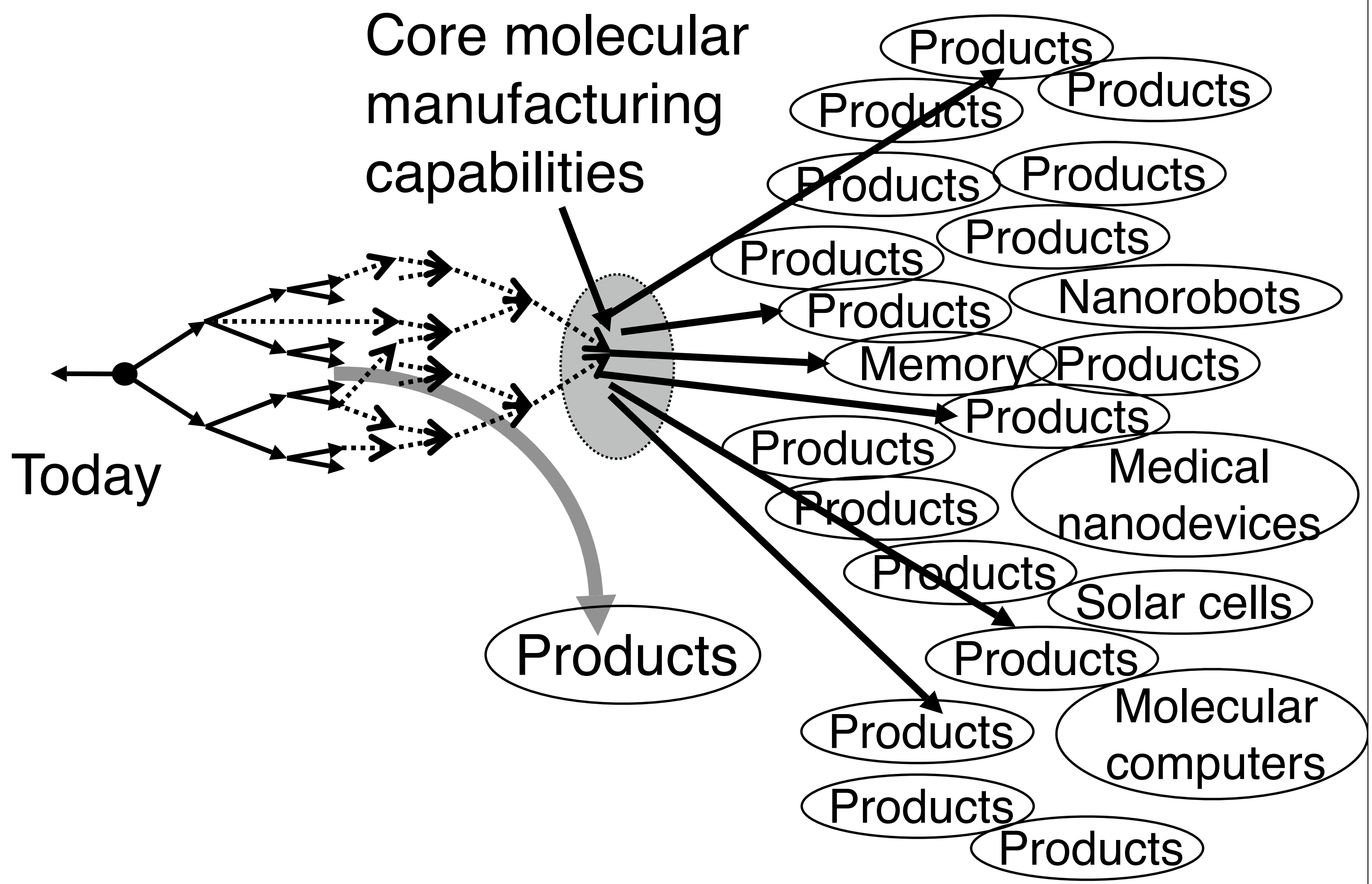
Diamond physical properties

Property	Diamond's value	Comments
Chemical reactivity		Extremely low
Hardness (kg/mm2)	9000	CBN: 4500 SiC: 4000
Thermal conductivity (W/cm-K)	20	Ag: 4.3 Cu: 4.0
Tensile strength (pascals)	3.5×10^9 (natural)	10^{11} (theoretical)
Compressive strength (pascals)	10^{11} (natural)	5×10^{11} (theoretical)
Band gap (ev)	5.5	Si: 1.1 GaAs: 1.4
Resistivity (W-cm)	10^{16} (natural)	
Density (gm/cm3)	3.51	
Thermal Expansion Coeff (K-1)	0.8×10^{-6}	SiO2: 0.5×10^{-6}
Refractive index	2.41 @ 590 nm	Glass: 1.4 - 1.8
Coeff. of Friction	0.05 (dry)	Teflon: 0.05

Achieving goals

- Backward chaining (Eric Drexler)
- Horizon mission methodology (John Anderson)
- Retrosynthetic analysis (Elias J. Corey)
- Shortest path and other search algorithms in computer science
- “Meet in the middle” attacks in cryptography

Overview


Core molecular
manufacturing
capabilities
Today
Products
Products
Products
Products
Products
Products
Products
Products
Products
Nanorobots
Memory
Products
Products
Products
Medical
nanodevices
Products
Products
Solar cells
Products
Molecular
computers
Products
Products
Products
Products

Single Bonds		Single Bonds *		Multiple Bonds	
H–H	**104.2**	**B–F**	**150**	**C=C**	**146**
C–C	**83**	**B–O**	**125**	**N=N**	**109**
N–N	**38.4**	**C–N**	**73**	**O=O**	**119**
O–O	**35**	**N–CO**	**86**	**C=N**	**147**
F–F	**36.6**	**C–O**	**85.5**	**C=O** (CO_2)	**192**
Si–Si	**52**	**O–CO**	**110**	**C=O** (aldehyde)	**177**
P–P	**50**	**C–S**	**65**	**C=O** (ketone)	**178**
S–S	**54**	**C–F**	**116**	**C=O** (ester)	**179**
Cl–Cl	**58**	**C–Cl**	**81**	**C=O** (amide)	**179**
Br–Br	**46**	**C–Br**	**68**	**C=O** (halide)	**177**
I–I	**36**	**C–I**	**51**	**C=S** (CS_2)	**138**
H–C	**99**	**C–B**	**90**	**N=O** (HONO)	**143**
H–N	**93**	**C–Si**	**76**	**P=O** ($POCl_3$)	**110**
H–O	**111**	**C–P**	**70**	**P=S** ($PSCl_3$)	**70**
H–F	**135**	**N–O**	**55**	**S=O** (SO_2)	**128**
H–Cl	**103**	**S–O**	**87**	**S=O** (DMSO)	**93**
H–Br	**87.5**	**Si–F**	**135**	**P=P**	**84**
H–I	**71**	**Si–Cl**	**90**	**P≡P**	**117**
H–B	**90**	**Si–O**	**110**	**C≡O**	**258**
H–S	**81**	**P–Cl**	**79**	**C≡C**	**200**
H–Si	**75**	**P–Br**	**65**	**N≡N**	**226**
H–P	**77**	**P–O**	**90**	**C≡N**	**213**

Strengths of hydrogen bonds

- O—H...:N (29 kJ/mol or 6.9 kcal/mol)
- O—H...:O (21 kJ/mol or 5.0 kcal/mol)
- N—H...:N (13 kJ/mol or 3.1 kcal/mol)
- N—H...:O (8 kJ/mol or 1.9 kcal/mol)

- C—C (347 kJ/mol or 83 kcal/mol)

Annotated bibliography on mechanosynthesis

(over 50 entries)

http://www.molecularassembler.com/Nanofactory/AnnBibDMS.htm

Hydrogen abstraction tools

Theoretical bibliography

•Michael Page, Donald W. Brenner, "Hydrogen abstraction from a diamond surface: *Ab initio* quantum chemical study using constrained isobutane as a model," ***J. Am. Chem. Soc.*** 113(1991):3270-3274.

•Charles B. Musgrave, Jason K. Perry, Ralph C. Merkle, William A. Goddard III, "Theoretical studies of a hydrogen abstraction tool for nanotechnology," ***Nanotechnology*** 2(1991):187-195; http://www.zyvex.com/nanotech/Habs/Habs.html

•Xiao Yan Chang, Martin Perry, James Peploski, Donald L. Thompson, Lionel M. Raff, "Theoretical studies of hydrogen-abstraction reactions from diamond and diamond-like surfaces," ***J. Chem. Phys.*** 99(15 September 1993):4748-4758.

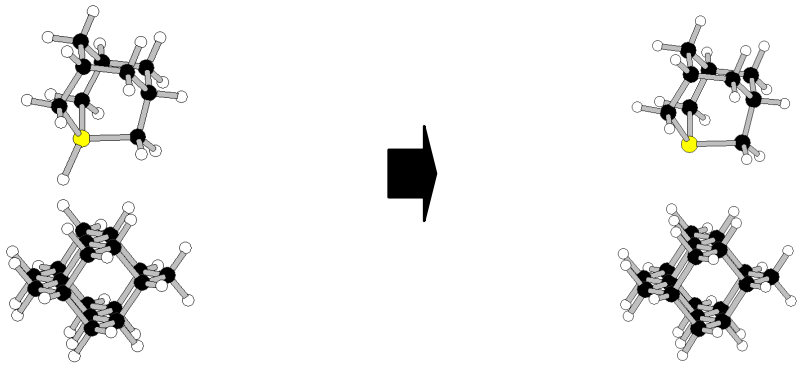
•Susan B. Sinnott, Richard J. Colton, Carter T. White, Donald W. Brenner, "Surface patterning by atomically-controlled chemical forces: molecular dynamics simulations," ***Surf. Sci.*** 316(1994):L1055-L1060.

•D.W. Brenner, S.B. Sinnott, J.A. Harrison, O.A. Shenderova, "Simulated engineering of nanostructures," ***Nanotechnology*** 7(1996):161-167; http://www.zyvex.com/nanotech/nano4/brennerPaper.pdf

•A. Ricca, C.W. Bauschlicher Jr., J.K. Kang, C.B. Musgrave, "Hydrogen abstraction from a diamond (111) surface in a uniform electric field," ***Surf. Sci.*** 429(1999):199-205.

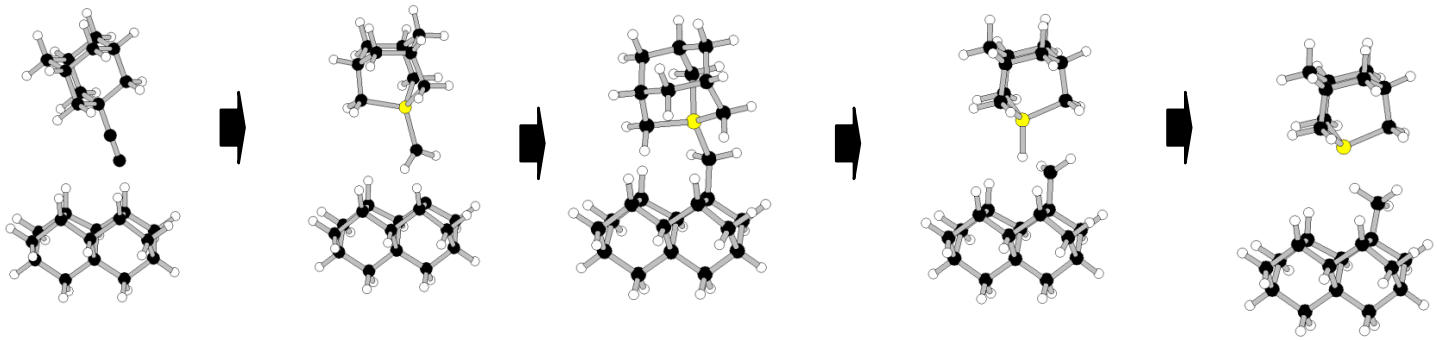
•Berhane Temelso, C. David Sherrill, Ralph C. Merkle, Robert A. Freitas Jr., "High-level *Ab Initio* Studies of Hydrogen Abstraction from Prototype Hydrocarbon Systems," ***J. Phys. Chem. A*** 110(28 September 2006):11160-11173; http://pubs.acs.org/cgi-bin/abstract.cgi/jpcafh/2006/110/i38/abs/jp061821e.html (abstract), http://www.MolecularAssembler.com/Papers/TemelsoHAbst.pdf (paper).

H donation



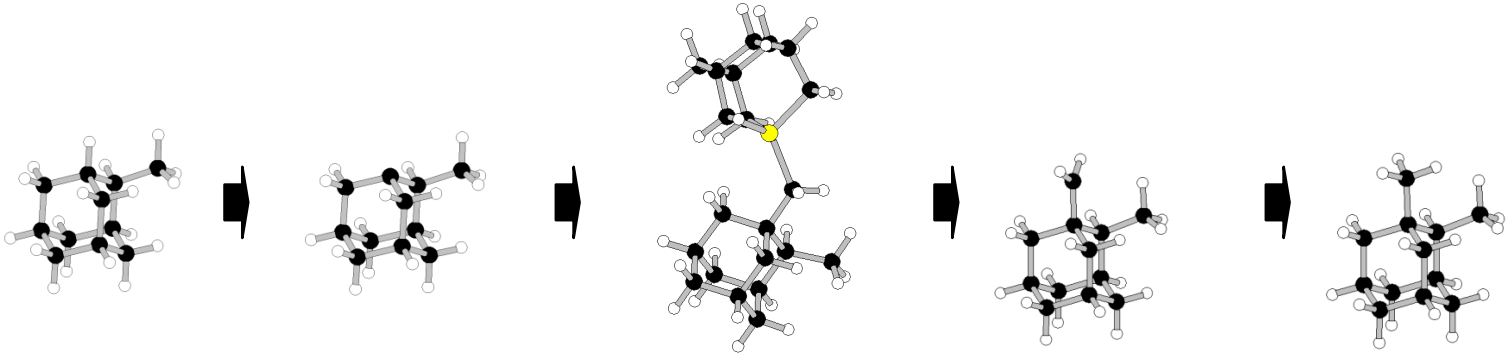
Hydrogen donation onto a C(110) surface radical.
-0.73 eV

C placement



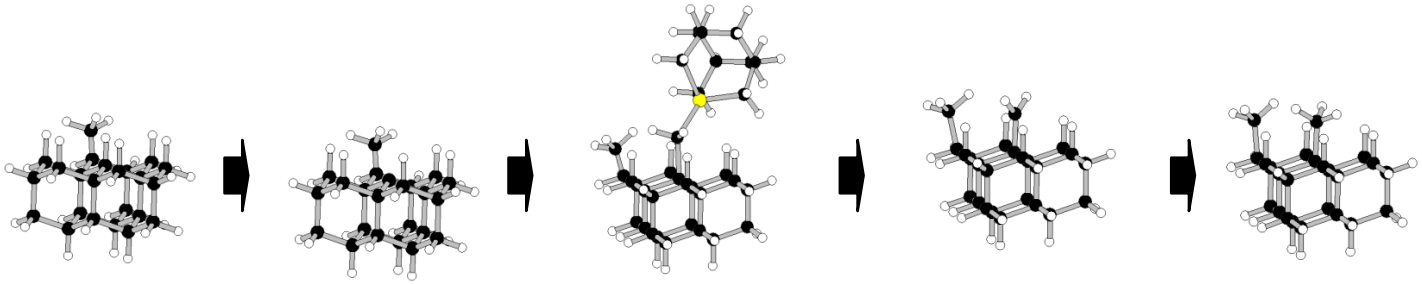
C placement on C(100) using GM tool
C radical addition to C radical -3.29 eV
(note undesired H abstraction by C radical from adjacent dimer, +0.55 eV barrier)
GeRad removal +2.66 eV (note Ge-C bond is “soft”)
HDon hydrogenate C radical -0.64 eV

C placement



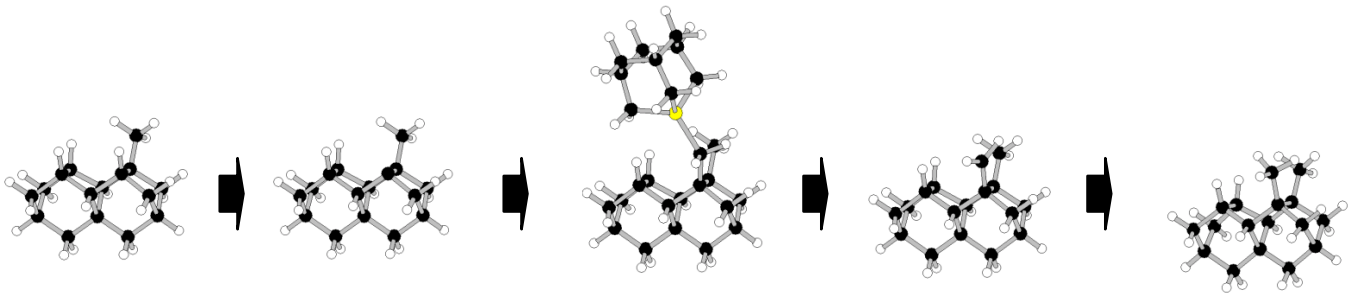
C placement on adamantane when sidewall site is occupied

C placement



C placement on adjacent site of C(111) surface

C placement

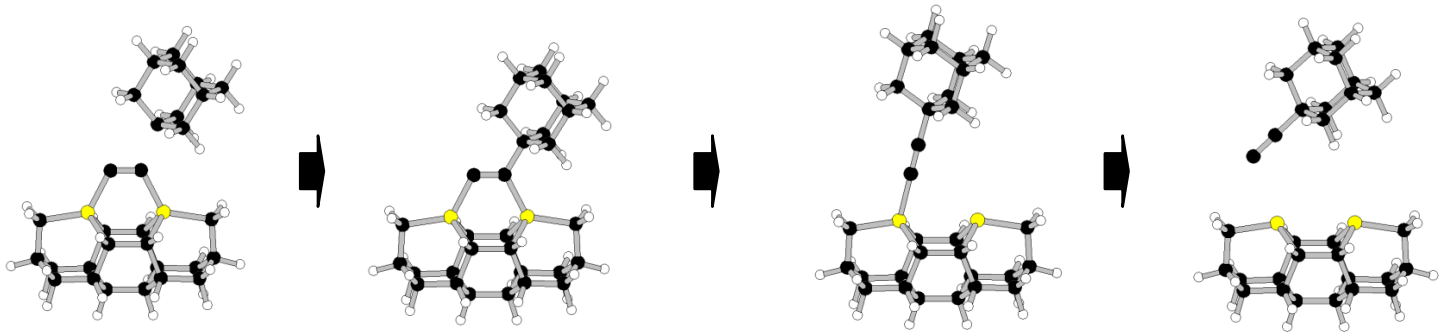


C placement on adjacent site of C(100) dimer

A strategy for the synthesis of stiff hydrocarbons

- Positional assembly (6 degrees of freedom)
- Highly reactive compounds (radicals, carbenes, etc)
- Inert environment (vacuum, noble gas) to eliminate side reactions

Making tools



Building HAbs from DimerP

Dimer placement

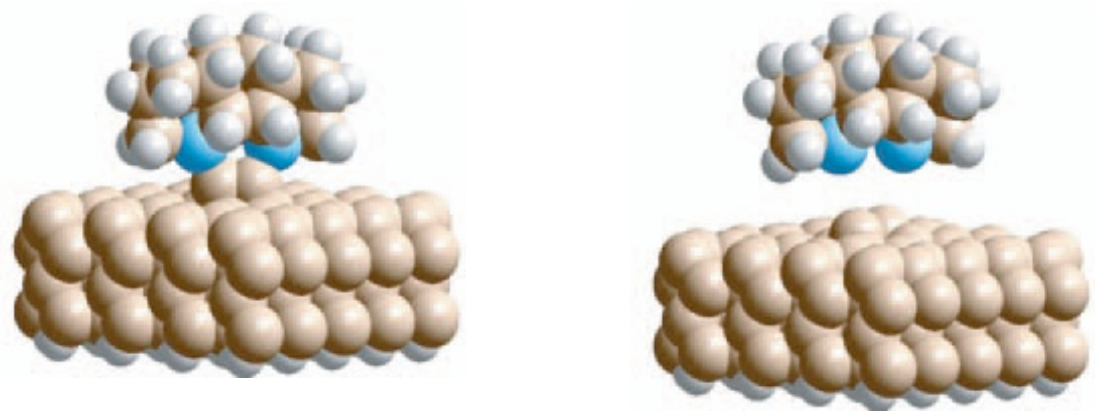
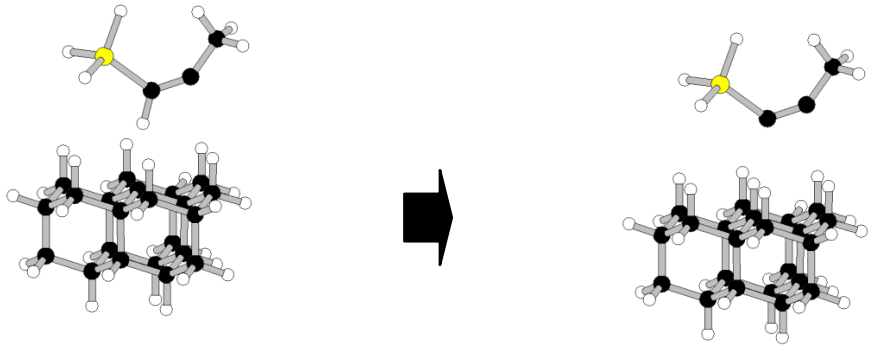


Fig. 2. Stepwise retraction simulation of Ge-based tool from clean diamond C(110) surface: (A) initial configuration (C in brown, H in white, Ge in blue); (B) ending configuration after 200 fs at 1.6 Å above starting position, at 300 K.

Peng et al., work done at Zyvex using VASP

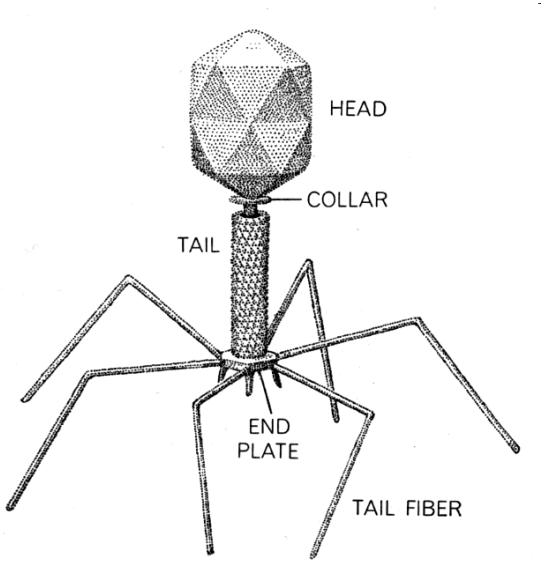
H donation



Hydrogen donation onto a C(111) surface radical.
-1.43 eV

Molecular machines

Self assembly of T4 Bacteriophage



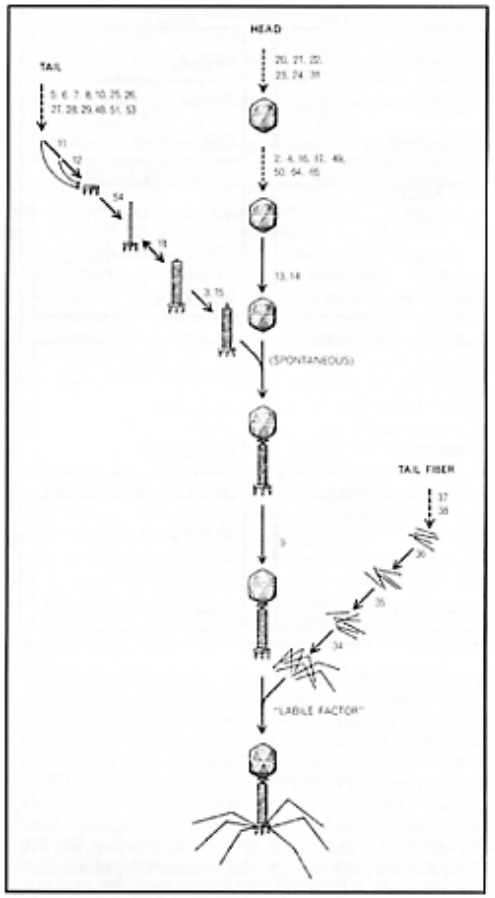


Figure 4.16. Self-assembly of bacteriophage T4 in ordered sequence from its individual component parts.[1769] (Copyright 1965 Scientific American)

A Minimal Toolset for Positional Diamond Mechanosynthesis

Journal of Computational and Theoretical Nanoscience Vol.5, 760–861, 2008

by Robert A. Freitas Jr. and Ralph C. Merkle

Bibliography of over 50 references on mechanosynthesis at
http://www.molecularassembler.com/Nanofactory/AnnBibDMS.htm

Mechanosynthesis

Reactants follow controlled trajectories to eliminate side reactions

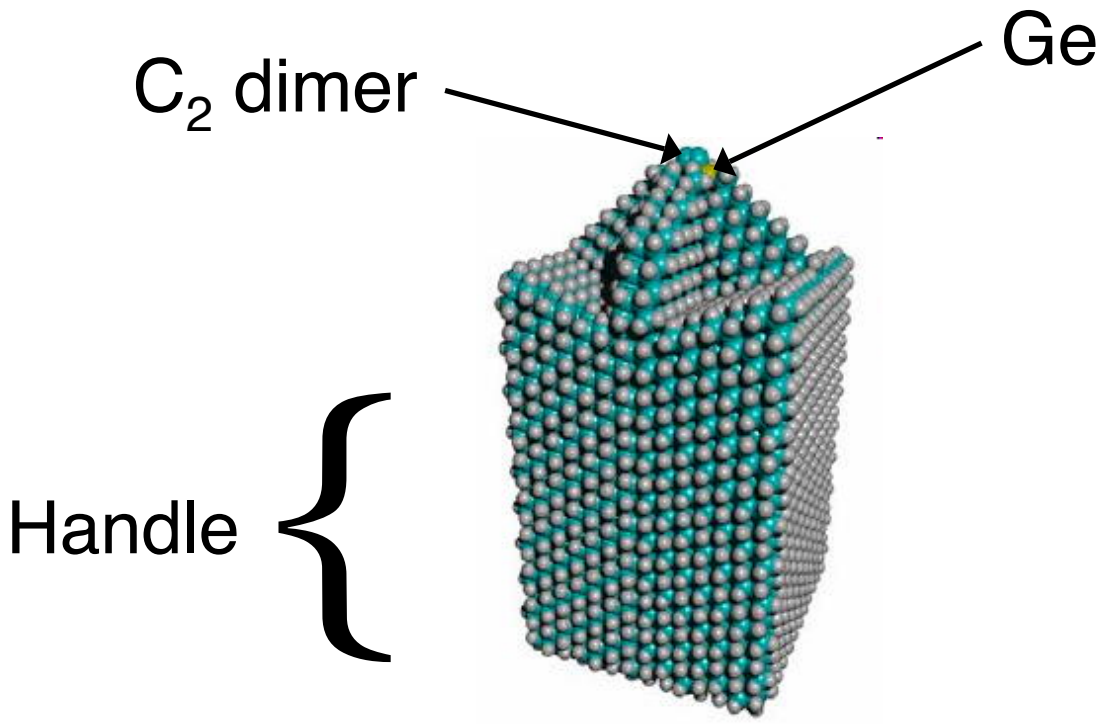
Extensive use of highly reactive (promiscuous) reactants

Fewer stronger bonds to achieve high strength

Inert environment (vacuum)

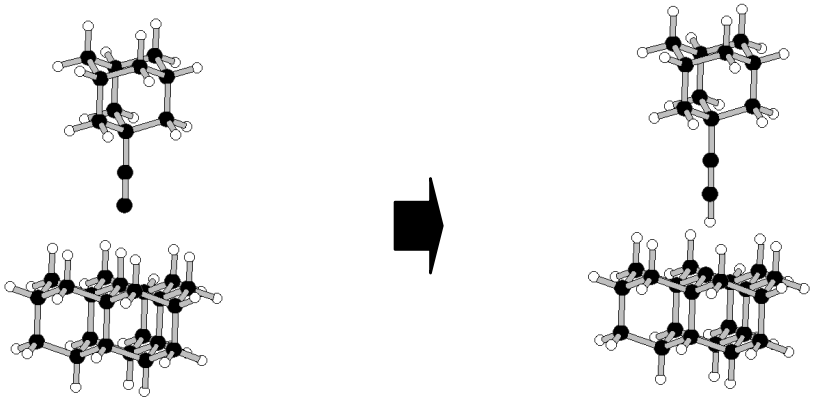
Solubility is not required

Adding carbon



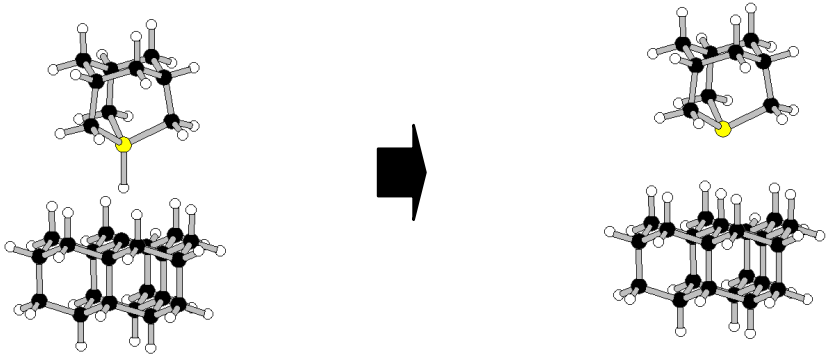
Dimer placement tool (DCB6-Ge)

H abstraction



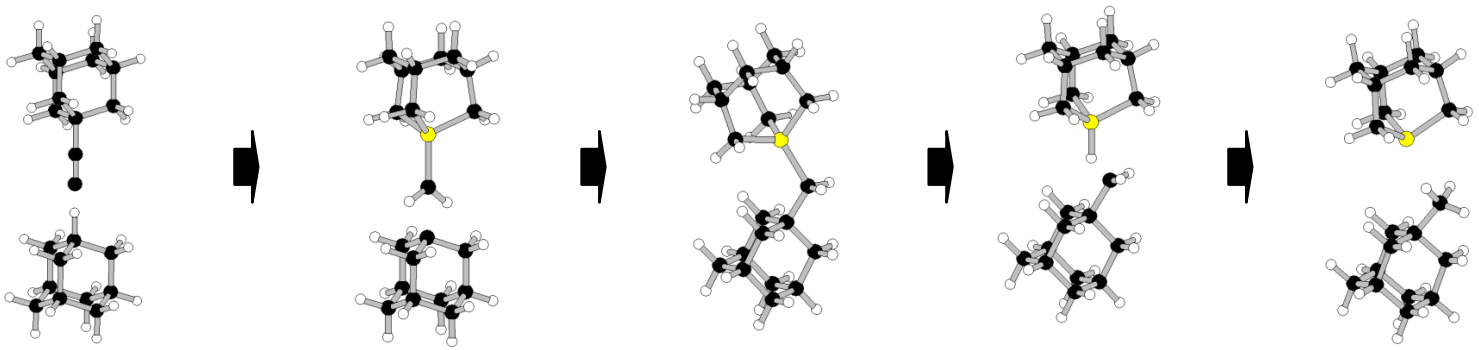
Hydrogen abstraction from a C(111) surface, creating a radical site.
-1.59 eV

H donation



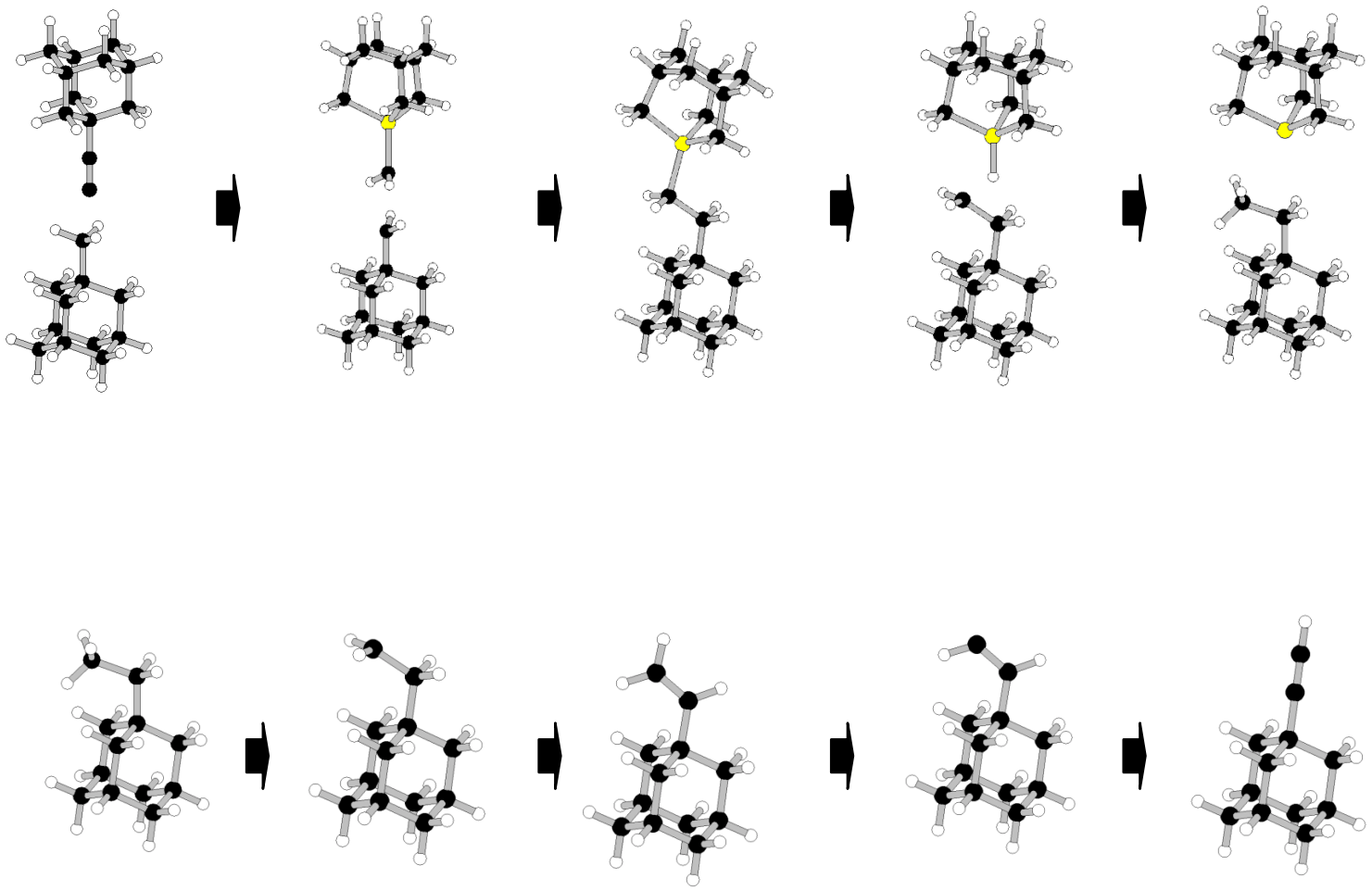
Hydrogen donation onto a C(111) surface radical.
-0.61 eV

C placement

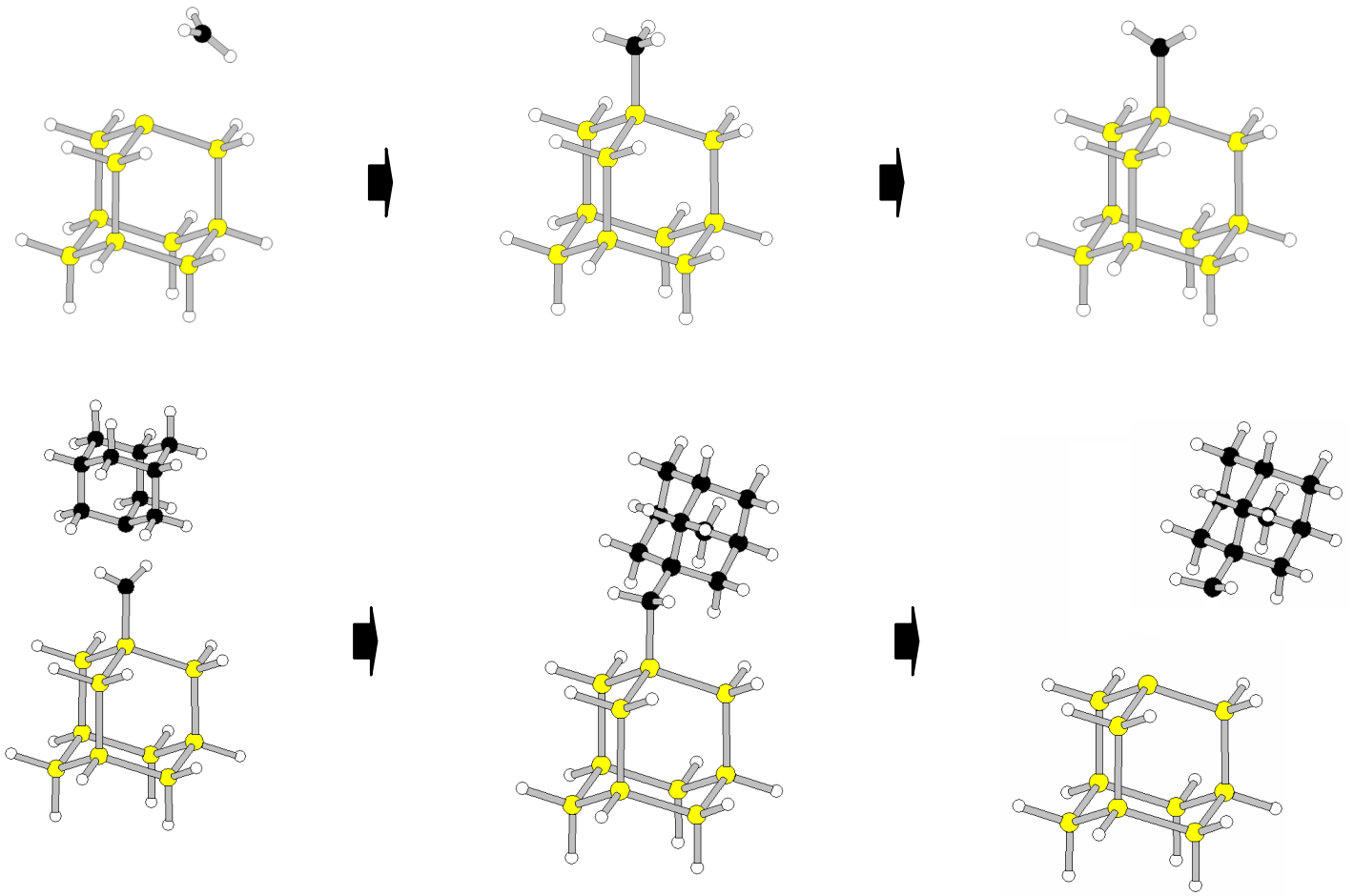


C placement on C(111) using GM tool
C radical addition to C radical -3.17 eV
(note undesired H abstraction by C radical from sidewall, +0.63 eV barrier)
GeRad removal +2.76 eV (note Ge-C bond is “soft”)
HDon hydrogenate C radical -0.70 eV

Making HAbst



Presentation surfaces



Reaction summary

- Abstract hydrogen with HAbst
- Donate hydrogen with HDon
- Recharge HAbst and HDon
- Add carbon to workpiece with GM tool
- Recharge GM tool (see paper)
- Tool synthesis sequences (see paper)