Historical Use of Calcium Catalysis

- Union Carbide-type Calcocene Catalyst (heterogenous, poorly defined)
- Used as a polymerization Catalyst

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Ph

Ph





SPS produced and commercialized by Idemitsu (metallocene catalyst)



Anionic polymerization of styrene by a well-defined Ca(II) species



Compound **3** effectively initiates the polymerization of styrene to produce syndiotactic polystyrene







Chain-end controlled mechanism



The chain-end inversion may limit the polymerization stereoselectivity



Mechanism of chain-end inversion





Alkene hydroamination reactions catalyzed by group 1 or 2 metal complexes



- Atom-efficient process used in industry
- Kinetically disfavored while thermodynamically allowed

Potential utility of a catalyst

Example:





Well-defined Calcium amido species for the intramolecular Hydroamination of aminoalkenes



Calcium-based catalyst



Mechanism





Enantiopure N-heterocycles are key components in numerous biologically active molecules



Calcium-mediated hydrophosphination of alkenes





Two classical mechanisms



Ph ₂ C=CH ₂	3-Ca (2.5)	none	PhH ₂ Si Me Ph	16	>98
Ph(H)C=CH2	3-Ca (2.5)	none	PhH ₂ Si Me Ph	<0.1	>98
Ph(Me)C=CH ₂	3-Ca (2.5)	none	PhH ₂ Si Me	24	20

Example of cat.





The role of polarity in Ca-mediated hydrosilylation of alkenes

7	Ph ₂ C=CH ₂	3-Ca (2.5)	THF	Ph Ph PhH ₂ Si	3	>98
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Reverse regioselectivity when the reaction is carried out in THF







Ring-opening polymerization of cyclic esters And cyclic carbonates by well-defined





Plastics World Production in 2006: 150 millions of tons

More than 99 % derives from petrochemistry

World Production of Biodegradable Polymers



Source: ADEME (Sustainable Development Agency)

Context: Expected decrease of petrochemical resources

Key Challenges: Development of *alternative* **materials from renewable and natural resources** that exhibit the essential properties of « classical » plastics (polyolefins) and may even outperform them.

Thus, the tremendous interest for biodegradable polymers from renewable resources over the last 10 years



The case of Poly(lactic acid)

Industrial Production: 140000 t. per year (from lactic acid)



First BP from renewable raw resources to be produced on an industrial scale

Structure of commonly commercialized PLA: Highly Isotactic



Poly (L-lactic) acid

 $T_g = 50 \ to \ 55 \ ^{\circ}C$ $T_m = 162 \ ^{\circ}C$

The stereoregularity of the PLA greatly improves its thermic and mechanical properties

Current Applications (other than medical): packaging, food containers, clothes



Research on PLA: Improvement of its properties And access to new materials

Better Control of the Chain length and of the Stereoregularity

- \Rightarrow Improve mechanical and thermal properties
- ➡ Access to potentially interesting new BPs







Through polymerization catalysis of lactide with a well-defined catalyst



Possibility of a controlled polymerization process affording polymers with well-defined chain length and stereoregularity

Current Approach: Ring-opening polymerization of lactides catalyzed by a well-defined metal complex M-OR



Dimers of lactic acid

Poly(lactic acid)

Possible Stereoregularities of polylactide







Usual mechanism: Coordination/insertion mechanism







Less active than compound **15**

6

SiMe₃



All these complexes are effective initiators of the ROP of L-lactide in the presence of an alcohol source



Chain-length-controlled PLA (« well-defined » properties)

«monomer activation»-type mechanism



Polymerization of Cyclic Esters Monomers: Acces to Synthetic Biodegradable polymers

• 2 representative examples



• Growing Interest in well-defined Poly(lactides) due to to their widespread applications

 \Box Biomedical and pharmaceutical applications (controlled drug delivery, medical implants \Box Promising degradable substitutes for petrochemical-based polyolefins \Box (D,L)-lactide, a cyclic dimer of lactic acid, which can be readily available from corn Well-defined AI Catalysts for Well-defined Poly(lactides)

Key issue: The obtention of stereoregular polymers with a controlled chain stereochemistry

 \Longrightarrow Well-defined and ligand-supported metal complexes as initiators



(*D*,*L*)-LA

Bourissou Chem. Rev, 2004, 104, 6147.

General Mechanism for the Ring-opening Polymerization of Lactides by Metal Alkoxides Complexes





Properties: New material, extremely high melting point (T_m up to 190 °C) And highly resistant

- Importance of the use of a well-defined and single-site catalyst

Le Borgne, A.; Vincens, V.; Jouglard, M.; Spassky, N. *Makromol. Chem., Macromol. Symp.* **1993**, **73**, 37. Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, **124**, **5938**.



Transesterification



Very common chain-transfer process in ring-opening polymerization of cyclic esters

- Detrimental to stereoregularity and chain control of the PLA

Enantioselective Polymerization

Principle: In an enantioselective polymerization, one enantiomer of a racemic monomer mixture is preferentially polymerized to give an optically active polymer (with a specific chain stereochemistry)



2 majors advantages: -Obtention of a chiral polymer with a controlled stereochemistry

-Monomer pool enantiomerically enriched

The use of enantiomerically pure Al Complexes: Enantioselective Polymerization of Lactides

• Interest: Access to optically active biodegradables polymers of potential interest



k_D/k_L = 20

Spassky Macromol. Chem. Phys. 1996, 197, 2627.



Stereocomplexes of PLA

Structure

PLA stereocomplexes

Extremely interesting BPs (very high Tm ~ 220-230°C) Excellent thermic and mechanical properties



Limitations: no straigthforward synthetic pathways available (Expensive material)

Applications: biomedical devices

poly(L-lactide) poly(D-lactide) Chain models of poly(L-lactide) and poly(D-lactide).

Left-handed Helicoidal chain Right-handed Helicoidal chain

Ikada et al. Macromolecules 1987

Formation of new materials via the formation of enantiomeric poly(L-LA) and poly(D-LA) block polymers



Due to chain transfer during the polymerization process

Isotactic Stereoblock Poly(lactide)

RRRRRRRRRRRRSSSSSSSSSSRRRRRRRRRR

Properties: extremely high melting point (Tm = 190 °C), highly resistant

A Related Example





(L)-lactide polymerized preferentially (optically active isotactic Poly(L-lactide)

At 50% conversion, ee (unreacted monomer) = 53% ee $k_L/k_D = 5.5$

Feijen, J. Am. Chem. Soc. 2003, 125, 11291.



> Isotactic Stereoblock Poly(lactides) with High $T_{\rm m}$



Organosilicon Chemistry



Organosilanes display many attractive properties:

- compared with other organometallic reagents they are much more moisture- and air-stable
- readily prepared from a wide range of often cheap starting materials
- low toxicity
- rich and diverse chemistry that can usually be rationalised by understanding a relatively small number of fundamental properties of Silicon



Silicon

Position in Periodic Table: Period 3, Group 14 (old group IV)

Electronegativity: 1.90 (Pauling scale)

more electropositive than carbon (2.55) and hydrogen (2.2)

metallic in character

C-Si and H-Si bonds are polarised:



bond	bond strength (kJ mol ^{–1)}	bond length (Å)		
Si–H	318 (in Me₃SiH)	1.48		
Si–C	318 (in Me₄Si)	1.85		
Si–O	452 (in Me₃SiOMe)	1.66		
Si–F	565 (in Me₃SiF)	1.57		

Stable compounds with a Si=Si double bond



West, Science 1981, 214, 1343.

A stable compound with Si-Si triple bond



First example of a isolable silyne species



Sekiguchi Science 2004, 305, 1755





No d orbitals involved !!!



Stabilisation of β-Positive Charge

Silicon is better at stabilising β -positive charge than is carbon.

This stabilisation effect is stereoelectronic in origin and often known as the β -Si-effect.¹



Maximum stabilisation requires the σ_{c-si} MO to align with the empty p AO on the adjacent carbocationic centre.







Stabilisation of α -Negative Charge

Carbanions with an α -silicon group are more stable than their carbon analogues:



is more stable than



2. Overlap between the filled σ orbital of the metal-carbon bond and the unfilled σ^*_{C-Si} orbital is energetically favourable. The larger coefficient on the silicon atom in the σ^* MO further improves the orbital overlap.





Stabilisation of α -Negative Charge

3. Si is a relatively large atom (van der Waals radius ~2.1 Å) and therefore readily polarised. *Induced dipoles* will also stabilise proximal negative charge.



This effect is probably the most important mechanism for stabilising α -negative charge.



Lewis Base/Lewis acid Interactions: Use in Organosilicon Chemistry

- The reaction of a Lewis acid with a Lewis base is typically thought to yield a less reactive Lewis adduct.



Example:



However, the formation of Lewis pair adducts may result into *an enhanced reactivity*.

The case of hypervalent Lewis adducts





In the five-coordinate Si anionic adduct:

Enhanced electrophilicity at the Si center

Enhanced nucleophilicity of the Si substituent (for instance, CF₃)



The formation of hypervalent Si species has been exploited in organosilicon chemistry

Electronic redistribution upon Lewis acid-base formation







Four rules (Guttman rules)

- 1) The smaller the D-A distance, the greater the induced lengthening of the A-X bonds
- 2) The longer the D-A bond, the greater the polarization of the D-A bond
- 3) The bond lengths increase with the coordination number of the central A atom
- 4) The D-L and A-X bonds will compensate for the changes in the electron density at D and A

The Lewis acidic center is often rendered **more electrophilic** while its ligands are **more nucleophilic**.

The addition of a Lewis base is thus a source of enhanced reactivity

Hypervalent Bonding Analysis: the case of Si





- Formation of three-center-four-electrons hybrid orbitals
- The HOMO is localized on the Si-L substituents





For the « activation » of silanes, F^- is typically used as a Lewis base.

Reaction of N-heterocyclic carbenes with Organosilanes





An example of catalytic application: Nucleophilic trifluoromethylation of ketones





Reduction of Carbonyl Compounds with Silyl Hydrides





DMPU



Charge distribution in hypervalent fluorosilanes



Initiating step: the NHC acts a strong Lewis base to form a hypervalent Si species.

Isolable Low valent silylene



First isolated and X-ray characterized silylene

West, JACS **1994**, *116*, 2691



Easy access to NHC-stabilized SiCl₂ silylene

Review on low valent Si species: J. Organomet. Chem. 2013, 730, 57.

Dimeric Silylene Species



Angew. Chem. Int. Ed. 2009, 48, 8536

Disilylene species (formally Si(I) species)





6 π -electrons (2 Si(III) centers) Planar C₄Si₂ ring

Chem. Commun. **2010**, *46*, 5873

Fundamental electronic properties of Carbenes



Carbenes: neutral compounds featuring a divalent carbon atom with only six electrons on its valence shell

- Four electronic configurations



- Ground-spin multiplicity: dictates the reactivity of the carbenes

Singlet carbenes: ambiphilic character, in principle Triplet carbenes: generally regarded as diradicals

- Ground-spin multiplicity is determined by the relative energy of the σ and p_{π} orbitals

- The nature of the $C_{\mbox{\scriptsize carbene}}$ substituents will be a determining factor

Role of the carbene substituents



Inductive Effects:

- $-\sigma$ -electron withdrawing substituents favors the singlet state
- $-\sigma$ -electron donating substituents favors the triplet state







- Mesomeric effects typically play a more significant role

$X = \pi$ -electron-donating substituent



Four-electrons three-centered π-system

- Stabilization of the C_{carbene} empty p_{π} By donation from the 2 nitrogens.

- Carbene lone pair stabilized by $\sigma\text{-electron-}$ withdrawing substituents



N-Heterocyclic Carbene (*NHC*) Chemistry



First isolation of stable *N*-heterocyclic carbene Arduengo 1991

JACS 1991, 113, 361.







Olefin Metathesis Grubbs, Nolan, Herrmann (1999) Suzuki Coupling Nolan, Glorius (2003)

NHC: Example of Olefin Metathesis Catalyst





Leading reviews: Acc. Chem. Res. 1999, 32, 913; Chem. Rev. 2000, 100, 39.

« Abnormal » Carbenes/mesoionic Carbenes



Review: Coord. Chem. Rev. 2013, 257, 755.









X = CI, Br









Access to Bis-carbene group 1 species and Chemical derivatization





Robinson, JACS **2010**, *132*, 14370.

For a review on NHC-bearing group 1and 2 species: *Chem. Rev.* **2014**, *114*, 8747.