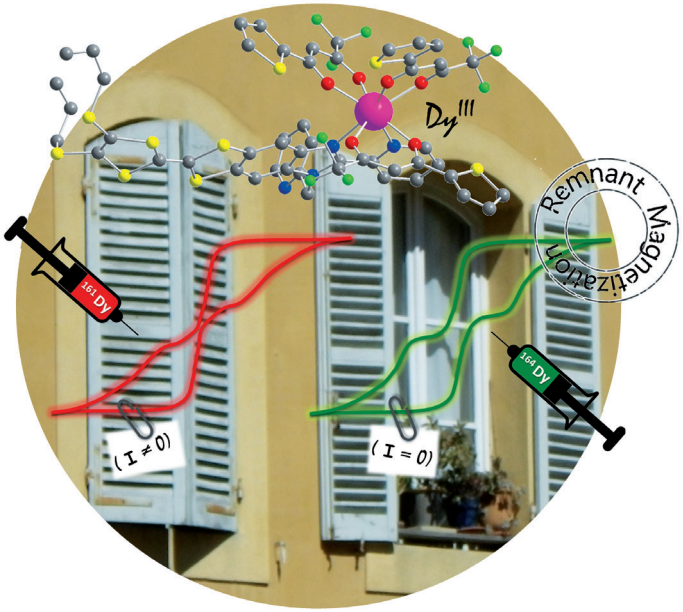
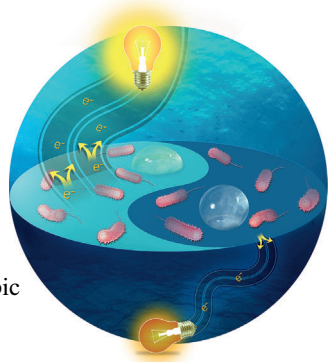
Angewandte International Edition Chemie

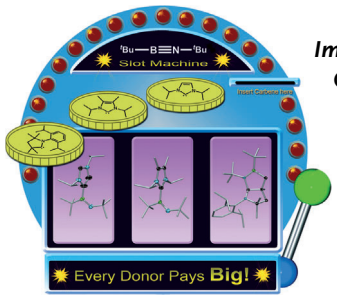


… in a mononuclear Dy-based single-molecule magnet (SMM) can be drastically reduced, improving the capability of the molecule to store magnetic information. As O. Cador and co-workers show in their Communication on page 1504 ff, this improvement is brought about by using isotopes of Dy^{III} that do not have a nuclear magnetic moment and by dilution of the SMM in a diamagnetic matrix. Combined, these strategies lead to the opening of the hysteresis loop in zero field, and the relaxation time is increased.



Electron Transfer

Extracellular electron transfer from living microbes can be regulated by altering the surface wettability of the electrode. In their Communication on page 1446 ff., H. Liu, Y. Zhu, et al. report that the electron transfer activity on a hydrophilic electrode is more than five times higher than that on a hydrophobic one.



Iminoborane Adducts

Carbene–iminoborane adducts are structural and isoelectronic congeners of the conventional imine functional group. H. Braunschweig and co-workers describe the reactions of these compounds in their Communication on page 1662 ff.

Zeolite Catalysts

Positron annihilation lifetime spectroscopy is used to probe pore connectivity of zeolites. A direct correlation with catalyst longevity in the conversion of methanol to hydrocarbons was observed by J. Pérez-Ramírez et al. in their Communication on page 1591 ff.

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... Italy has the record of the most ancient university in Europe, but it is also one of the European countries with the lowest investments in research and education. Despite monstrous and inefficient bureaucracy and other obstacles, Italy is producing some outstanding research.
Read more in the Editorial by Roberta Sessoli.

Editorial

R. Sessoli* ——— **1374 – 1375**

Italian Research at a Turning Point: An Opportunity that Cannot Be Missed

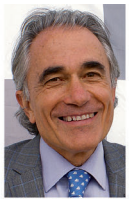
Service

Spotlight on Angewandte's Sister Journals **1394 – 1397**

News

Real Sociedad Española de Química Prizes 2014 ——— **1398 – 1399**


L. M. Liz-Marzán


F. Albericio


M. C. Carreño


M. Costas


M. L. López-Rodríguez

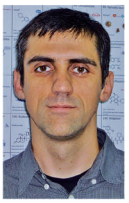

E. Ortí


P. H. Dixneuf


A. Caballero


A. de la Escosura


M. Tortosa


R. Vicente

Author Profile

"My favorite food is Mongolian-style barbeque lamb. If I won the lottery, I would go traveling. …"
This and more about Chunhai Fan can be found on page 1400.

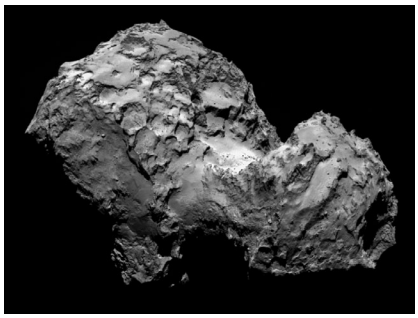
Chunhai Fan _____ **1400**

Minireviews

Symmetry Breaking

I. Myrgorodska, C. Meinert, Z. Martins, L. Le Sergeant d'Hendecourt, U. J. Meierhenrich* _____ **1402 – 1412**

Molecular Chirality in Meteorites and Interstellar Ices, and the Chirality Experiment on Board the ESA Cometary Rosetta Mission



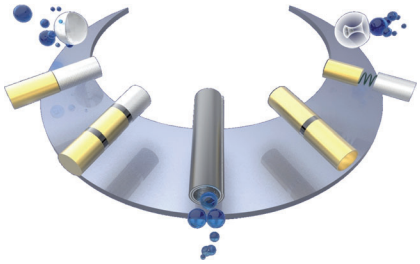
Back to where it all began: In November 2014, the Philae lander detached from the Rosetta orbiter to soft-land on the surface of a cometary nucleus. Philae is equipped with a device for the identification of chiral molecules in cometary ices. Crucial insight into the origin of the homochirality of biomolecules is expected (image: ESA/Rosetta/MPS for OSIRIS Team MPS/UPD/LAM/IAA/SSO/INTA/UPM/DASP/IDA).

Reviews

Micro- and Nanomotors

S. Sánchez,* L. Soler, J. Katuri _____ **1414 – 1444**

Chemically Powered Micro- and Nanomotors



Moving down in the world: Chemically powered micro- and nanomotors are small devices that are self-propelled by catalytic reactions in fluids. Remotely guided nanomotors can transport cargo to desired targets, drill into biomaterials, sense their environment, mix or pump fluids, and clean polluted water.

For the USA and Canada:
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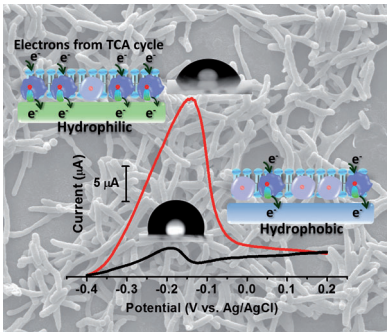
Communications

Hydrophobic or hydrophilic: The electron flow from living microbes can be simply regulated by altering the surface wettability of the electrodes at a fixed external potential. The extracellular electron transfer activity on a hydrophilic electrode is shown to be more than five times higher than that on a hydrophobic one. TCA = tricarboxylic acid.

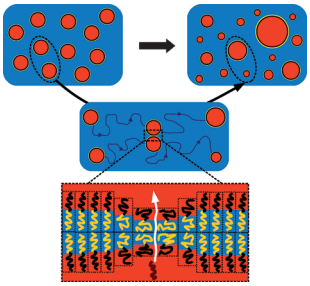


Electrochemistry

C. M. Ding, M. L. Lv, Y. Zhu,* L. Jiang, H. Liu* ——— 1446 – 1451

Wettability-Regulated Extracellular Electron Transfer from the Living Organism of *Shewanella loihica* PV-4

Frontispiece

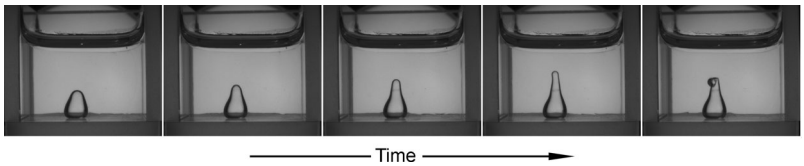


Another pathway for coarsening of emulsion is uncovered, besides coalescence and Ostwald ripening, that is termed contact ripening (top). Its mechanism consists of an exchange of oil molecules during collisions of droplets (middle). The key step is the synchronous thinning of each surfactant layer, through which oil molecules can cross the interface (bottom).

Colloid Chemistry

K. Roger,* U. Olsson, R. Schweins, B. Cabane ——— 1452 – 1455

Emulsion Ripening through Molecular Exchange at Droplet Contacts



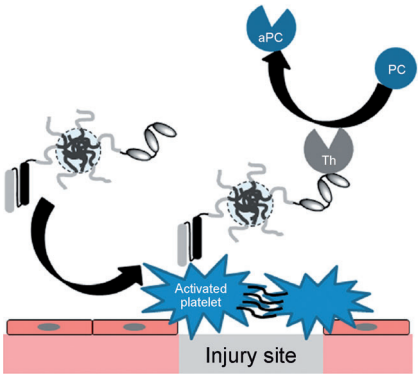
Sprouting droplets: With increasing time, tubes are observed to sprout from water droplets with rigid membranes formed from colloidal particles trapped on the liquid–liquid interface. This is driven by an internal over-pressure which arises as a result of a minority constituent on the outside of the droplet that preferentially partitions into the water inside the membrane.

Liquid–Liquid Interfaces

M. Graužinytė, J. Forth, K. A. Rumble, P. S. Clegg* ——— 1456 – 1460

Particle-Stabilized Water Droplets that Sprout Millimeter-Scale Tubes

Site-specific: An activated platelet-specific antibody and antithrombotic protein were site-specifically conjugated to the corona of protein nanomicelles for efficient detection and inhibition of thrombus formation. These multifunctional protein micelles provide a promising approach to the site-specific delivery of a potent antithrombotic agent, thus reducing the dose and bleeding risk. aPC = activated protein C, Th = thrombin.



Bioconjugation

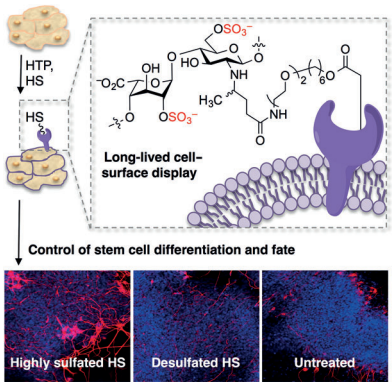
W. Kim, C. Haller, E. Dai, X. Wang, C. E. Hagemeyer, D. R. Liu, K. Peter, E. L. Chaikof* ——— 1461 – 1465

Targeted Antithrombotic Protein Micelles

Cell-Surface Engineering

A. Pulsipher, M. E. Griffin, S. E. Stone, L. C. Hsieh-Wilson* ——— 1466 – 1470

Long-Lived Engineering of Glycans to Direct Stem Cell Fate

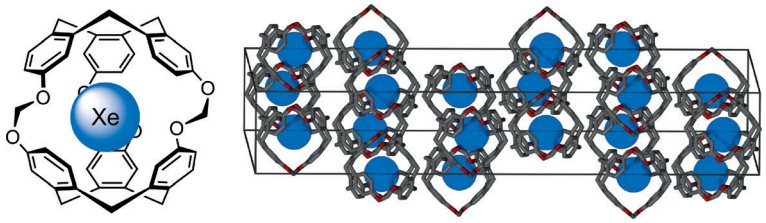


Sweet display: A method for the long-lived presentation of specific glycans on cell surfaces is reported. HaloTag proteins (HTP) were utilized to covalently attach defined heparan sulfate (HS) structures to embryonic stem cell membranes. Highly sulfated HS induced differentiation into neuronal cell types, thus demonstrating the potential of glycan engineering to drive important physiological processes.

Noble Gas Clathrates

A. I. Joseph, S. H. Lapidus, C. M. Kane, K. T. Holman* ——— 1471 – 1475

Extreme Confinement of Xenon by Cryptophane-111 in the Solid State

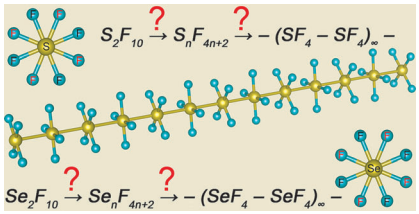


Imprisoning a noble: Xenon gas is effectively imprisoned, at temperatures of up to 300 °C, by a trigonal crystalline phase of the discrete container molecule (±)-cryptophane-111. The seemingly unprecedented kinetic stability of the gas clathrate can be attributed in part to its crystal packing.

Chemical Bonding

I. A. Popov, B. B. Averkiev, A. A. Starikova, A. I. Boldyrev,* R. M. Minyaev,* V. I. Minkin* ——— 1476 – 1480

Assessing the Viability of Extended Nonmetal Atom Chains in M_nF_{4n+2} (M = S and Se)



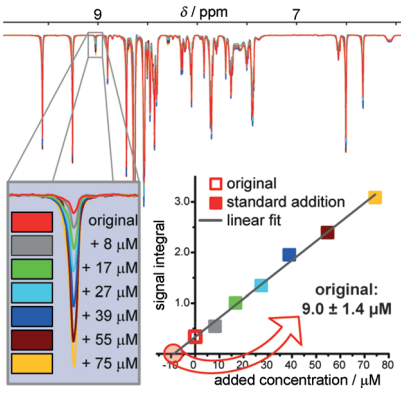
No end in sight: The viability of extended chains of nonmetal atoms was assessed theoretically on the basis of molecular models M_nF_{4n+2} (M = S or Se, yellow; F turquoise) and corresponding solid-state systems exhibiting direct S–S or Se–Se bonding. The proposed molecules were found to be minima for S_nF_{4n+2} systems with $n = 2$–9 and for selenium analogues with $n \leq 6$, and the -$(SF_4–SF_4)_\infty$- structure, unlike -$(SeF_4–SeF_4)_\infty$-, was found to be dynamically stable.

NMR Spectroscopy

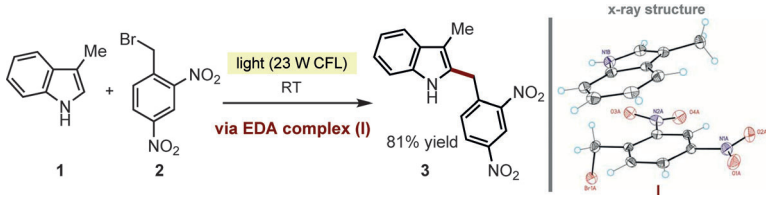
N. Eshuis, B. J. A. van Weerdenburg, M. C. Feiters, F. P. J. T. Rutjes, S. S. Wijmenga, M. Tessari* 1481 – 1484

Quantitative Trace Analysis of Complex Mixtures Using SABRE Hyperpolarization

Quantitative trace analysis: Nuclear spin hyperpolarization of small molecules in complex mixtures is achieved by signal amplification by reversible exchange (SABRE). The resulting signal enhancements allow quantification of compounds present at low micromolar concentrations in a few single-scan NMR experiments.



Inside Cover

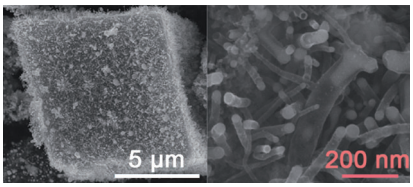


Mutual aid: The electron-rich indole **1** and the electron-accepting bromide **2** readily aggregate to form the photoactive electron donor–acceptor (EDA) complex **I**. Upon irradiation with light, the alkylation product **3** is formed with high yield (see scheme; CFL = compact fluorescence lamp). The synthetic consequences of this discovery along with the X-ray structure of the relevant EDA complex are discussed.

Photochemistry

S. R. Kandukuri, A. Bahamonde, I. Chatterjee, I. D. Jurberg, E. C. Escudero-Adán, P. Melchiorre* ——— **1485 – 1489**

X-Ray Characterization of an Electron Donor–Acceptor Complex that Drives the Photochemical Alkylation of Indoles



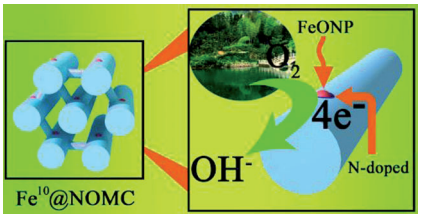
High capacity anodes: A tin/carbon hierarchical structure was designed, in which some of the nanosized Sn particles are anchored on the tips of carbon nanotubes that are rooted on the surfaces of micro-sized hollow carbon cubes while other Sn nanoparticles are encapsulated in the hollow carbon cubes. Such a unique structure allows the Sn particles to accommodate the volume change upon lithiation.

Lithium-Ion Batteries

X. K. Huang, S. M. Cui, J. B. Chang, P. B. Hallac, C. R. Fell, Y. T. Luo, B. Metz, J. W. Jiang, P. T. Hurley, J. H. Chen* ——— **1490 – 1493**

A Hierarchical Tin/Carbon Composite as an Anode for Lithium-Ion Batteries with a Long Cycle Life

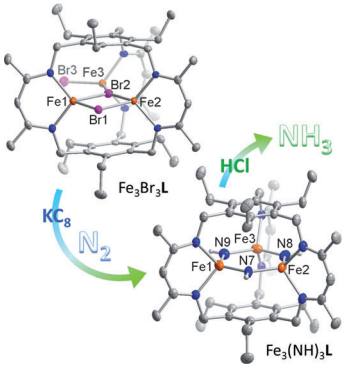
N-enriched and Fe-embedded ordered mesoporous carbon electrocatalysts were fabricated from an ionic liquid precursor by hard template synthesis. This strategy provides a high surface area and populated Fe-N active sites with synergetic interaction for an optimized Fe^{10}@NOMC catalyst. The catalyst shows excellent electrocatalytic efficiency and durability for the oxygen reduction in alkaline media.



Heterogeneous Catalysis

Z. L. Li, G. L. Li, L. H. Jiang, J. L. Li, G. Q. Sun,* C. G. Xia,* F. W. Li* ——— **1494 – 1498**

Ionic Liquids as Precursors for Efficient Mesoporous Iron-Nitrogen-Doped Oxygen Reduction Electrocatalysts



A trinuclear iron(II) complex, Fe_3Br_3**L** in which **L** is a cyclophane bridged by three β-diketiminate arms, reacts with KC_8 under a dinitrogen atmosphere to form complex $Fe_3(NH)_3$**L** among other products. Reactions with $^{14}N_2$ and $^{15}N_2$ confirm atmospheric N_2 reduction, and ammonia was detected by the indophenol assay. IR and Mössbauer spectroscopy as well as elemental analysis support the assignment that the reduction product contains protonated N-atom bridges.

Iron Clusters

Y. Lee, F. T. Sloane, G. Blondin, K. A. Abboud, R. García-Serres,* L. J. Murray* ——— **1499 – 1503**

Dinitrogen Activation Upon Reduction of a Triiron(II) Complex

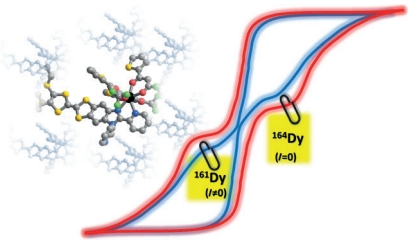
Single-Molecule Magnets

F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab, O. Cador* ——— 1504 – 1507

Magnetic Memory in an Isotopically Enriched and Magnetically Isolated Mononuclear Dysprosium Complex

Front Cover

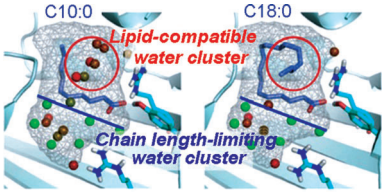
DIY magnetism: The quantum tunneling in a mononuclear Dy-based complex, which already behaves as a single-molecule magnet (SMM), can be drastically reduced, improving the capability of the molecule to store magnetic information. This improvement is brought about by using isotopes of Dy^{III} without a nuclear magnetic moment, thus suppressing the hyperfine interaction, and by dilution of the SMM in a diamagnetic matrix, thus cancelling the internal field.



Molecular Dynamics

S. Matsuoka, S. Sugiyama, D. Matsuoka, M. Hirose, S. Lethu, H. Ano, T. Hara, O. Ichihara, S. R. Kimura, S. Murakami, H. Ishida, E. Mizohata, T. Inoue, M. Murata* ——— 1508 – 1511

Water-Mediated Recognition of Simple Alkyl Chains by Heart-Type Fatty-Acid-Binding Protein



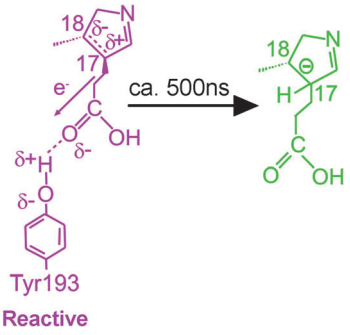
Distinguishing fatty acids: The heart-type fatty-acid-binding protein was shown to preferentially incorporate U-shaped fatty acids of C10–C18 by using a chain-length-limiting water cluster. This mechanism was uncovered by ultrahigh-resolution X-ray crystallography as well as energy calculations of the coexisting water molecules with the WaterMap program.

Enzyme Catalysis

D. J. Heyes,* S. J. O. Hardman, T. M. Hedison, R. Hoeven, G. M. Greetham, M. Towrie, N. S. Scrutton* ——— 1512 – 1515

Excited-State Charge Separation in the Photochemical Mechanism of the Light-Driven Enzyme Protochlorophyllide Oxidoreductase

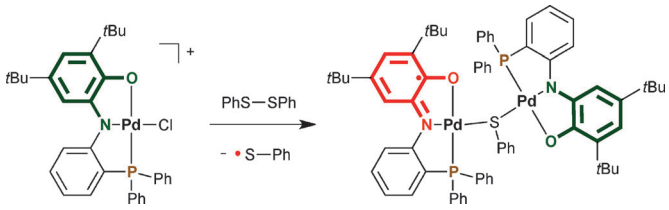
Shining light on enzyme catalysis: Time-resolved spectroscopy has shown how light energy is harnessed to power catalysis in the light-driven enzyme protochlorophyllide oxidoreductase. Excited-state interactions between the enzyme and substrate result in a polarized and highly reactive double bond to trigger a subsequent nucleophilic attack of NADPH.



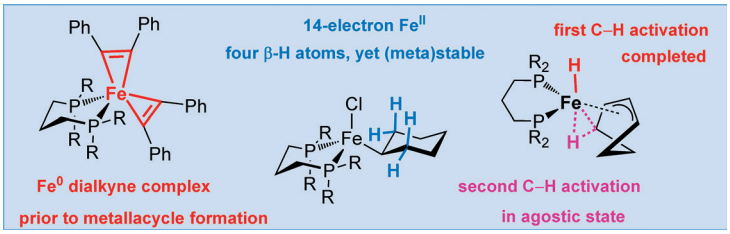
Redox-Active Ligands

D. L. J. Broere, L. L. Metz, B. de Bruin, J. N. H. Reek, M. A. Siegler, J. I. van der Vlugt* ——— 1516 – 1520

Redox-Active Ligand-Induced Homolytic Bond Activation



PNO duet: The redox-active pincer ligand PNO, which has a flanking phosphine group, can coordinate to Pd^{II} in various oxidation states. One-electron reduction from paramagnetic [PdCl(PNO)] generates a competent reagent for the homolytic bond activation of disulfides through ligand-to-substrate single-electron transfer. The resulting dinuclear Pd species, which has a monothiolate bridgehead, shows well-defined ligand mixed valency in the solid state.

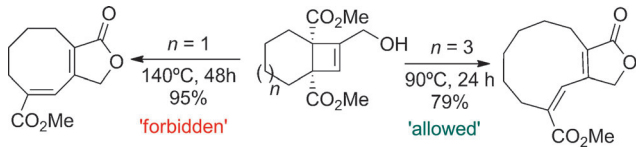


Trio con brio: Several unorthodox complexes of high relevance for the understanding of iron-catalyzed C–H activation and C–C bond formation have been obtained. These include a surrogate of an intermediate in [2+2+2] cycloaddition reactions, a 14e $[L_2Fe(X)R]$ species that is (meta)stable despite its potential for β-H elimination, and an iron allyl hydride complex formed by two consecutive C–H activation events mediated by a single iron center.

Organoiron Complexes

A. Casitas, H. Krause, R. Goddard, A. Fürstner* ——— **1521 – 1526**

Elementary Steps of Iron Catalysis: Exploring the Links between Iron Alkyl and Iron Olefin Complexes for their Relevance in C–H Activation and C–C Bond Formation

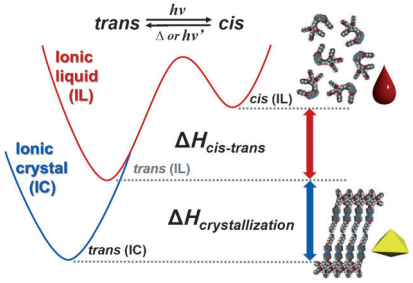


***cis* or *trans*?** The thermal electrocyclic ring opening of a homologous series of [*n*.2.0]-fused bicyclic systems proceeds via cyclic *cis*,*trans*-dienes, in accordance with the Woodward–Hoffmann rules. Highly strained smaller cyclic dienes (≤9 members) undergo isomerization to the stable *cis*,*cis* system, while larger cyclic *cis*,*trans* dienes (≥10 members) are isolable.

Photochemistry

M. J. Ralph, D. C. Harrowven, S. Gaulier, S. Ng, K. I. Booker-Milburn* ——— **1527 – 1531**

The Profound Effect of the Ring Size in the Electrocyclic Opening of Cyclobutene-Fused Bicyclic Systems

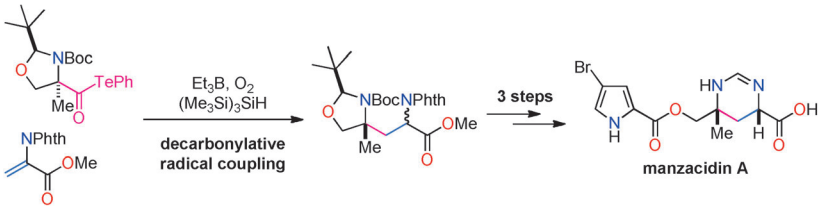


Going through a phase: ICs of azobenzene derivatives show a photoinduced IC–IL phase transition (photoliquefaction) upon UV irradiation, and the resulting *cis*-azobenzene ILs are reversibly photocrystallized by illumination with visible light. The photoliquefaction of ICs is accompanied by a significant increase in ionic conductivity at ambient temperature and holds potential as energy storage materials.

Phase Transitions

K. Ishiba, M-a. Morikawa,* C. Chikara, T. Yamada, K. Iwase, M. Kawakita, N. Kimizuka* ——— **1532 – 1536**

Photoliquefiable Ionic Crystals: A Phase Crossover Approach for Photon Energy Storage Materials with Functional Multiplicity



Upon activation by Et_3B and O_2 at ambient temperature, α-aminoacyl tellurides were readily converted into α-amino carbon radicals through facile decarbonylation, which then reacted intermolecularly with acrylates or glyoxylic oxime ethers to generate various γ-amino and α,β-diamino acids. This mild and powerful coupling method was also applied to the synthesis of gabapentin and the natural product (−)-manzacidin A.

Radical Reactions

M. Nagatomo, H. Nishiyama, H. Fujino, M. Inoue* ——— **1537 – 1541**

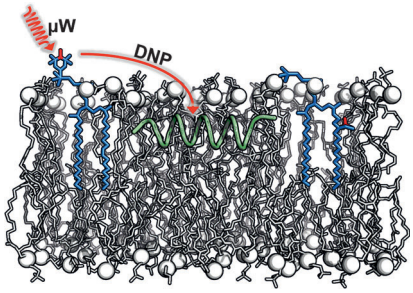
Decarbonylative Radical Coupling of α-Aminoacyl Tellurides: Single-Step Preparation of γ-Amino and α,β-Diamino Acids and Rapid Synthesis of Gabapentin and Manzacidin A

Solid-State NMR Spectroscopy

A. N. Smith, M. A. Caporini, G. E. Fanucci, J. R. Long* ——— 1542 – 1546

A Method for Dynamic Nuclear Polarization Enhancement of Membrane Proteins

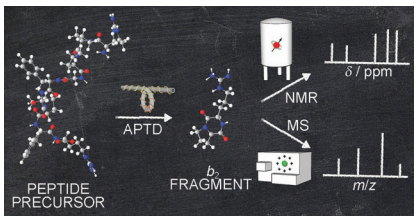
Large signal enhancements were observed for a membrane-embedded peptide throughout the lipid bilayer in dynamic nuclear polarization (DNP) magic-angle spinning solid-state NMR experiments when spin-labeled lipids were used as a polarizing agent. The enhancement gradient typically observed with the use of water-soluble biradicals was diminished.



Gas-Phase Ion Chemistry

P. Liu, R. G. Cooks,* H. Chen* ——— 1547 – 1550

Nuclear Magnetic Resonance Structure Elucidation of Peptide b_2 Ions



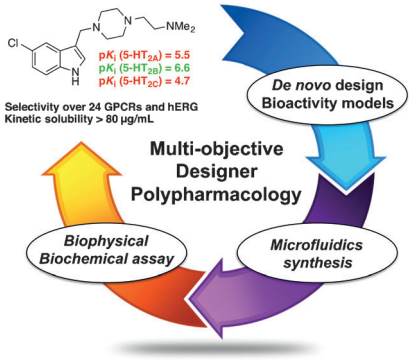
Fragmentation of peptide ions: Atmospheric pressure thermal dissociation-(APTD) based preparative mass spectrometry was used to collect gas-phase peptide b_2 fragments for structural elucidation by NMR spectroscopy. This strategy will be applicable to the elucidation of many difficult fragment ion structures in both fundamental ion chemistry studies and in applied proteomics research.

Drug discovery

T. Rodrigues, N. Hauser, D. Reker, M. Reutlinger, T. Wunderlin, J. Hamon, G. Koch, G. Schneider* ——— 1551 – 1555

Multidimensional De Novo Design Reveals 5-HT_{2B} Receptor-Selective Ligands

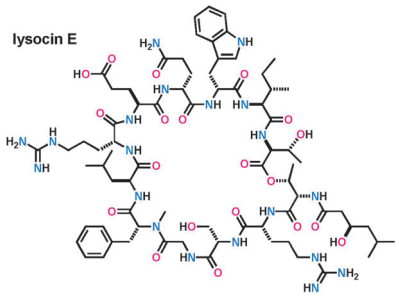
Multi-objective design: Multidimensional de novo design generated innovative and nanomolar-potent 5-HT_{2B}-selective antagonists. Computational bioaffinity prediction for full target panels and microfluidics-assisted synthesis facilitated their discovery. Our results suggest that such integrated discovery platforms will find further applicability in swift prototyping of drug candidates.



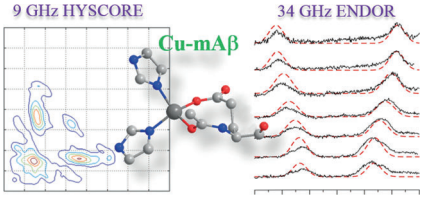
Natural Product Synthesis

M. Murai, T. Kaji, T. Kuranaga, H. Hamamoto, K. Sekimizu, M. Inoue* ——— 1556 – 1560

Total Synthesis and Biological Evaluation of the Antibiotic Lysocin E and Its Enantiomeric, Epimeric, and N-Demethylated Analogues



The antibacterial macrocyclic peptide lysocin E and its enantiomeric, epimeric, and N-demethylated analogues were synthesized by a full solid-phase strategy. Significantly, the antibacterial activity of the unnatural enantiomer was comparable to that of the natural isomer, suggesting the absence of chiral recognition in its mode of action.



Pulsed EPR spectroscopy in conjunction with specific isotope labeling was employed to investigate the structure of copper-murine amyloid peptides. This first detailed structural characterization shows that Ala2, Glu3, His6, and His14 are directly coordinated with the copper ion in murine amyloid β peptides at pH 8.5.

Binding Modes in Peptides

D. Kim, J. K. Bang, S. H. Kim* ——— **1561 – 1564**

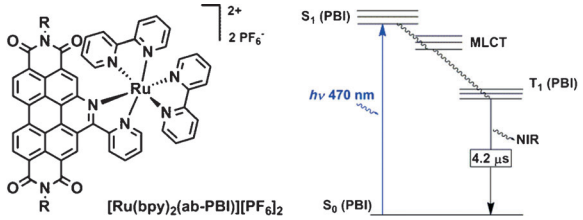
Multi-Frequency, Multi-Technique Pulsed EPR Investigation of the Copper Binding Site of Murine Amyloid β Peptide

Use visible light! The direct α-arylation of cyclic and acyclic ethers with heteroarenes can be achieved at room temperature through a photoredox-mediated C–H functionalization pathway. This mild, visible-light-driven protocol allows direct access to medicinal pharmacophores of broad utility using feedstock substrates and a commercial photocatalyst. SET = single-electron transfer.

C–H Functionalization

J. Jin, D. W. C. MacMillan* ——— **1565 – 1569**

Direct α-Arylation of Ethers through the Combination of Photoredox-Mediated C–H Functionalization and the Minisci Reaction

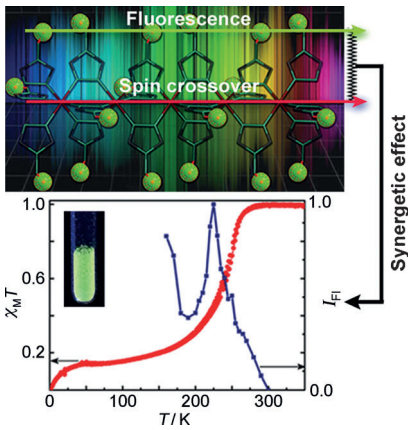


The attachment of a ruthenium(II) or iridium(III) metal complex to the perylene core of an azabenzannulated perylene bisimide (ab-PBI) leads to strong phosphorescence out of the PBI triplet state after visible-light absorption. The near-IR phosphorescence of the ruthenium complex has a quantum yield (Φ_p) of 11%, which is remarkably high in comparison to other NIR emitters.

Phosphorescent Complexes

M. Schulze, A. Steffen,* F. Würthner* ——— **1570 – 1573**

Near-IR Phosphorescent Ruthenium(II) and Iridium(III) Perylene Bisimide Metal Complexes



Two hybrid materials assembled from a 1D spin-crossover structure and the fluorophores 1-pyrenecarboxaldehyde and Rhodamine B were prepared. A synergetic effect between spin crossover and fluorescence was proposed.

Hybrid Materials

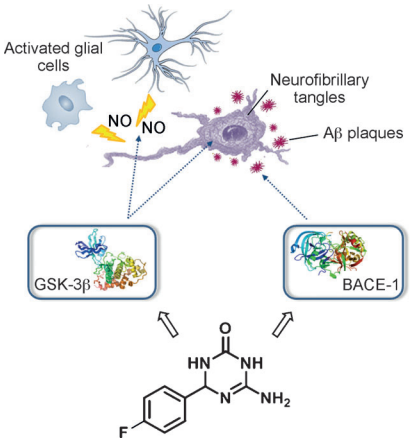
C.-F. Wang, R.-F. Li, X.-Y. Chen, R.-J. Wei, L.-S. Zheng, J. Tao* ——— **1574 – 1577**

Synergetic Spin Crossover and Fluorescence in One-Dimensional Hybrid Complexes

Drug Discovery

F. Prati, A. De Simone, P. Bisignano, A. Armirotti, M. Summa, D. Pizzirani, R. Scarpelli, D. I. Perez, V. Andrisano, A. Perez-Castillo, B. Monti, F. Massenzio, L. Polito, M. Racchi, A. D. Favia, G. Bottegoni, A. Martinez, M. L. Bolognesi,* A. Cavalli* _____ **1578 – 1582**

Multitarget Drug Discovery for Alzheimer's Disease: Triazinones as BACE-1 and GSK-3β Inhibitors

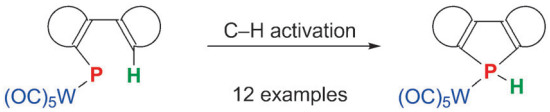


Two for one: Alzheimer's disease is a complex multifactorial syndrome which calls for the development of multitarget drugs. Accordingly, triazinones are reported here as the first molecule class which is able to simultaneously modulate BACE-1 and GSK-3β activity. Such dual-target inhibitors, by acting against two crucial enzymes in the neurotoxic pathways, might represent a breakthrough in the quest for disease-modifying drugs.

C–H Activation

X. Wei, Z. Lu, X. Zhao, Z. Duan,* F. Mathey* _____ **1583 – 1586**

Synthesis of Annelated Phospholes through Intramolecular C–H Activation by Monovalent Phosphorus



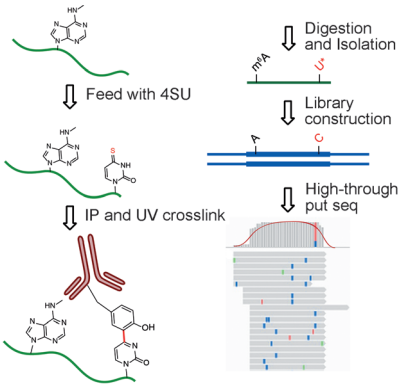
Proximity matters: Electrophilic terminal phosphinidene complexes (left, with Ar-Ar being biaryl or an analogue thereof) undergo a spontaneous insertion of the P atom into the vicinal C–H bond to give annelated phospholes. The latter compounds are valuable precursors for the preparation of a variety of optoelectronic devices.

RNA Modification

K. Chen, Z. Lu, X. Wang, Y. Fu, G.-Z. Luo, N. Liu, D. Han, D. Dominissini, Q. Dai, T. Pan, C. He* _____ **1587 – 1590**

High-Resolution N^6-Methyladenosine (m^6A) Map Using Photo-Crosslinking-Assisted m^6A Sequencing

Modification sites at N^6-methyladenosine (m^6A) can be more accurately defined with a photo-crosslinking-assisted m^6A sequencing strategy. It was used to obtain a high-resolution map of m^6A in a human transcriptome. 4SU = 4-thiouridine, IP = immunoprecipitation.

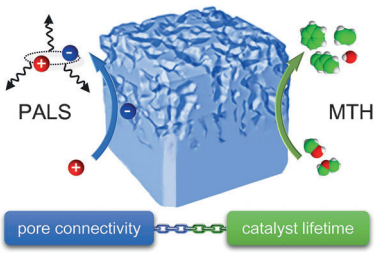


Heterogeneous Catalysis

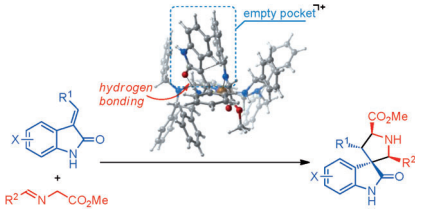
M. Milina, S. Mitchell, D. Cooke, P. Crivelli, J. Pérez-Ramírez* **1591 – 1594**

Impact of Pore Connectivity on the Design of Long-Lived Zeolite Catalysts

Back Cover



Well connected? The sensitivity of positron annihilation lifetime spectroscopy (PALS) to subtleties in the pore connectivity of hierarchical zeolite catalysts that arise from variations in the synthesis enables rationalization of their distinct lifetime in the conversion of methanol to hydrocarbons (MTH). The findings have huge implications for the manufacturing efficiency and performance of these and other advanced porous materials.

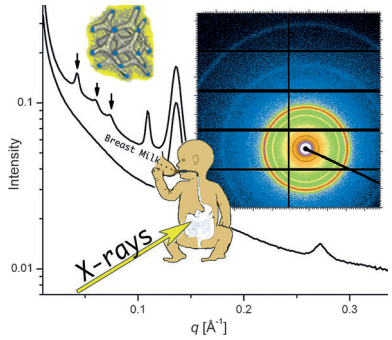


Dual activation system: A bis(imidazolidine)pyridine (PyBidine)–Cu(OTf)$_2$ complex catalyzes the *endo*-selective [3+2] cycloaddition of methyleneindolinones with imino esters to afford spiro[pyrrolidin-3,3′-oxindole]s in up to 98% *ee*. X-ray analysis and DFT calculations suggest that an intermediate Cu enolate of the imino ester reacts with the methyleneindolinone, which is activated by NH-hydrogen bonding with the PyBidine–Cu(OTf)$_2$ catalyst.

Asymmetric Catalysis

T. Arai,* H. Ogawa, A. Awata, M. Sato, M. Watabe, M. Yamanaka* _ **1595 – 1599**

PyBidine–Cu(OTf)$_2$-Catalyzed Asymmetric [3+2] Cycloaddition with Imino Esters: Harmony of Cu–Lewis Acid and Imidazolidine-NH Hydrogen Bonding in Concerto Catalysis

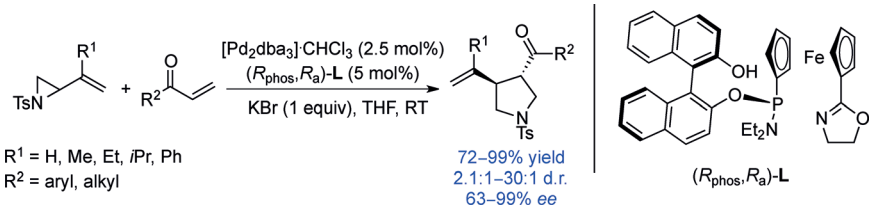


Baby fat: An infant's complete diet, human breast milk, is the key to its development and survival. The self-assembly of the lipid digestion products inside the breast milk fat droplet drives structure formation with a high internal surface area. The structure formation is necessarily linked to its function as a carrier for poorly water-soluble molecules in the digestive tract of the infant.

Lipids

S. Salentinig,* S. Phan, A. Hawley, B. J. Boyd* _____ **1600 – 1603**

Self-Assembly Structure Formation during the Digestion of Human Breast Milk

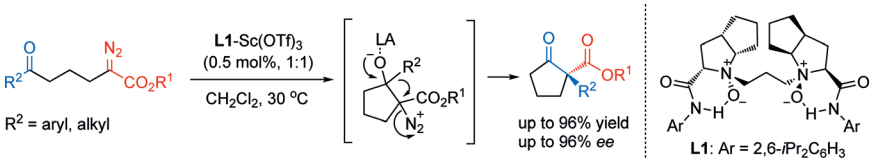


Ring to ring: The title reaction of vinyl aziridines and alkenes with a single activator was realized. The presence of the substituent on the vinyl group of the vinyl aziridine plays a key role in determining the stereochemical outcome of the reaction. dba = dibenzylidene acetone, Ts = 4-toluenesulfonyl.

Asymmetric Catalysis

C.-F. Xu, B.-H. Zheng, J.-J. Suo, C.-H. Ding,* X.-L. Hou* ___ **1604 – 1607**

Highly Diastereo- and Enantioselective Palladium-Catalyzed [3+2] Cycloaddition of Vinyl Aziridines and α,β-Unsaturated Ketones



A chiral *N*,*N*′-dioxide–Sc(OTf)$_3$ complex catalyzes the asymmetric intramolecular homologation of simple ketones with α-diazoesters. This method gives access to chiral cyclic α-aryl/alkyl β-ketoesters with an all-carbon quaternary stereocenter. The reaction proceeds under mild reaction conditions through an intramolecular addition/rearrangement process, thereby generating the β-ketoesters in high yield and enantiomeric excess.

Asymmetric Catalysis

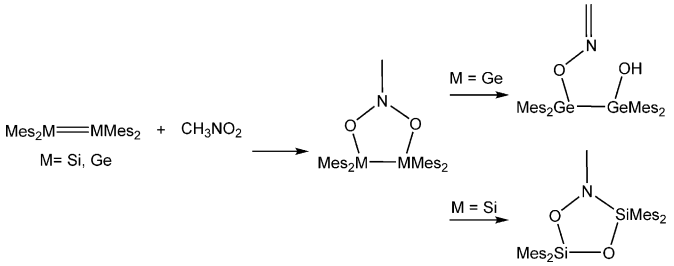
W. Li, F. Tan, X. Y. Hao, G. Wang, Y. Tang, X. H. Liu, L. L. Lin, X. M. Feng* _____ **1608 – 1611**

Catalytic Asymmetric Intramolecular Homologation of Ketones with α-Diazoesters: Synthesis of Cyclic α-Aryl/Alkyl β-Ketoesters

[3+2] Cycloaddition Reactions

N. Y. Tashkandi, F. Parsons, J. Guo, K. M. Baines* ——— 1612–1615

Addition of Nitromethane to a Disilene and a Digermene: Comparison to Surface Reactivity and the Facile Formation of 1,3,2-Dioxazolidines

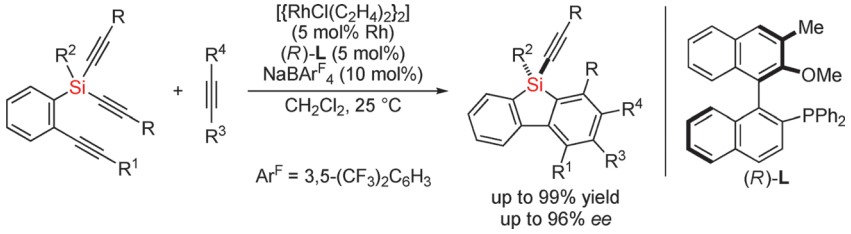


Nitromethane addition to tetramesityldisilene and tetramesityldigermene leads to the formation of 1,3,2,4,5-dioxazadisil- and digermolidine ring systems, respectively. The 1,3,2,4,5-dioxazadisilolidine isomerizes to the 1,4,2,3,5-dioxazadisilolidine ring system, whereas the 1,3,2,4,5-dioxazadigermolidine undergoes ring opening to the isomeric oxime.

Asymmetric Catalysis

R. Shintani,* C. Takagi, T. Ito, M. Naito, K. Nozaki* ——— 1616–1620

Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles by Enantioselective [2+2+2] Cycloaddition



Silicon cycles: An axially chiral monophosphine ligand is employed in the Rh-catalyzed reaction between silicon-containing prochiral triynes and internal alkynes to form silicon-stereogenic dibenzosiloles with high yields and enantioselectivities. A germanium-stereogenic dibenzogermole is also prepared by this method.

DOI: 10.1002/anie.201580514

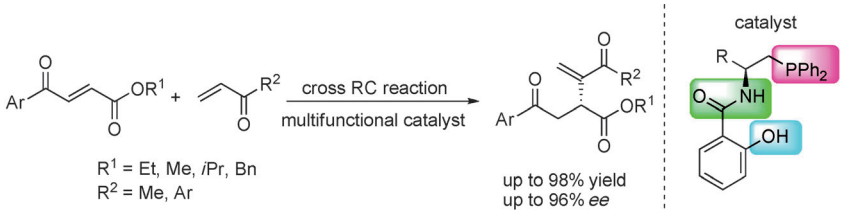
Flashback: 50 Years Ago . . .

Giulio Natta, who shared the 1963 Nobel Prize in Chemistry with Karl Ziegler, contributed a Review on the analogies between the stereochemical properties of macromolecules and those of classic organic cyclic compounds. In another Review, Dieter Seebach discussed the properties of three- and four-membered polycyclic systems, in particular tetrahedrane, Dewar benzene, prismane, and cubane. Seebach published a Minireview on geminal disubstitution in the 50th Jubilee Issue of *Angewandte Chemie International Edition* (see *Angew. Chem. Int. Ed.* **2014,** *50*, 96).

Hubert Schmidbaur (former Chairman of the Editorial Board of *Angewandte Chemie*) contributed three Communications on gallium-containing compounds. The first was on the synthesis of dichlorogallane $HGaCl_2$, which was formed by the reaction of trimethylsilane with gallium trichloride. The second report was on organoheterosilanes $Me_3SiOXMe_2$ and Me_3COXMe_2 (X = Al, Ga, or In), which occur as dimers that have a four-membered ring structure, and the third on the synthesis of trimethylaluminum trimethylphosphorus oxide and trimethylarsenic trimethylgallium oxide. Schmidbaur's Review on argentophilic interactions is currently in press (see *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201405936).

Hermann Stetter, after whom the Stetter reaction was named, described a new synthesis of the adamantane derivatives substituted in the 3-position, which were constructed by the cyclization of 3-methylenebicyclo[3.3.1]nonan-7-one or 3,7-dimethylenebicyclo[3.3.1]nonane in the presence of acids. This method could also be used to synthesize adamantane-containing polymers.

Read more in Issue 5/1965.

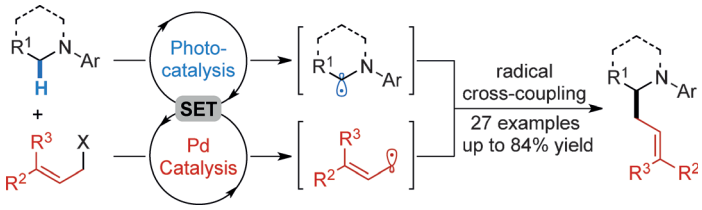


A cat. with handles: A multifunctional chiral Lewis base catalyst mediates the highly enantioselective intermolecular cross Rauhut–Currier (RC) reaction of different active olefins. The RC products were obtained in excellent yields and high chemo- and enantioselectivity. The reaction could be performed on a gram scale with a catalyst loading of 1 mol%.

Rauhut–Currier Reaction

X. Dong, L. Liang, E. Li, Y. Huang* ——— **1621 – 1624**

Highly Enantioselective Intermolecular Cross Rauhut–Currier Reaction Catalyzed by a Multifunctional Lewis Base Catalyst

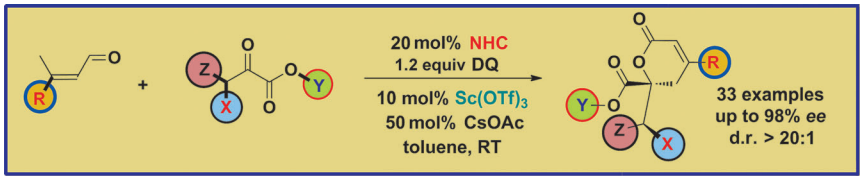


Double up: The title reaction was accomplished by merging palladium catalysis and visible-light photoredox catalysis. The catalytic generation of an allyl radical from the corresponding π-allylpalladium intermediate was realized without additional metal reducing reagents for the first time. Various α-allylation products of amines were achieved in high yields by radical cross-coupling under mild reaction conditions. SET = single-electron transfer.

Synthetic Methods

J. Xuan, T.-T. Zeng, Z.-J. Feng, Q.-H. Deng, J.-R. Chen, L.-Q. Lu,* W.-J. Xiao,* H. Alper ——— **1625 – 1628**

Redox-Neutral α-Allylation of Amines by Combining Palladium Catalysis and Visible-Light Photoredox Catalysis

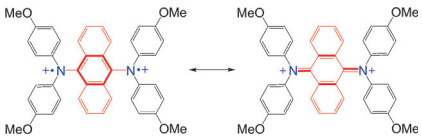


Enantioenriched δ-lactones were accessed by an intermolecular dynamic kinetic resolution of β-halo-α-ketoesters in an oxidation/lactonization sequence. The process generates two contiguous stereocenters with remarkable diastereoselectivity through the cooperative catalysis of an N-heterocyclic carbene and a Lewis acid. DQ = 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (oxidant).

Lactone Synthesis

Z.-J. Wu, F.-Y. Li, J. Wang* ——— **1629 – 1633**

Intermolecular Dynamic Kinetic Resolution Cooperatively Catalyzed by an N-Heterocyclic Carbene and a Lewis Acid



Dications: A series of bis[*N*,*N*-di-(4-methoxylphenyl)amino]arene dications have been synthesized and characterized. It was found that they are singlets in the ground state and that their diradical character is dependent on the bridging moiety. The work provides a nitrogen analogue of Thiele's hydrocarbon with a considerable diradical character.

Diradicals

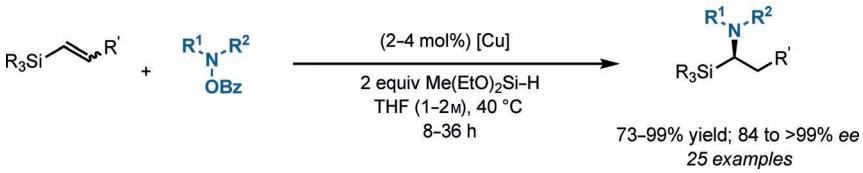
Y. Su, X. Wang, Y. Li, Y. Song, Y. Sui, X. Wang* ——— **1634 – 1637**

Nitrogen Analogues of Thiele's Hydrocarbon

Asymmetric Synthesis

N. Niljianskul, S. Zhu,
S. L. Buchwald* ——— 1638 – 1641

Enantioselective Synthesis of α-Aminosilanes by Copper-Catalyzed Hydroamination of Vinylsilanes



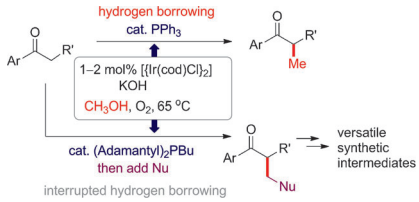
Versatile vinylsilanes: The use of a Cu catalyst, diethoxymethylsilane as a stoichiometric reductant, and *O*-benzoylhydroxylamines as the electrophilic nitrogen source allows the synthesis of α-aminosilanes. This highly enantio- and regioselective hydroamination reaction is compatible with differentially substituted vinylsilanes, thereby providing access to amino acid mimics and other valuable chiral organosilicon compounds.

Synthetic Methods

D. Shen, D. L. Poole, C. C. Shotton,
A. F. Kornahrens, M. P. Healy,
T. J. Donohoe* ——— 1642 – 1645

Hydrogen-Borrowing and Interrupted-Hydrogen-Borrowing Reactions of Ketones and Methanol Catalyzed by Iridium

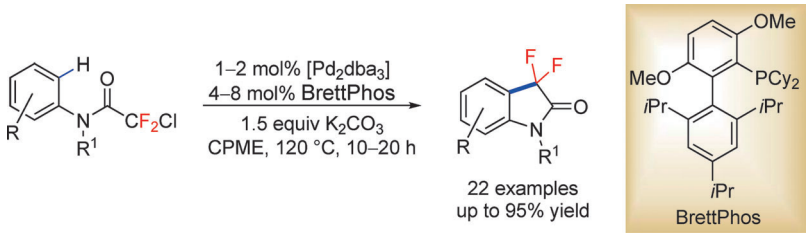
On loan: [{Ir(cod)Cl}$_2$] facilitates hydrogen-borrowing reactions of ketone enolates with methanol at 65 °C as described. Performing the reaction under an oxygen atmosphere aids the process, and when combined with a bulky monodentate phosphine ligand, interrupts the catalytic cycle by preventing enone reduction. The addition of pro-nucleophiles to the reaction mixture completes a one-pot methylenation/conjugate addition method.



C–H Activation

S.-L. Shi, S. L. Buchwald* ——— 1646 – 1650

Palladium-Catalyzed Intramolecular C–H Difluoroalkylation: Synthesis of Substituted 3,3-Difluoro-2-oxindoles

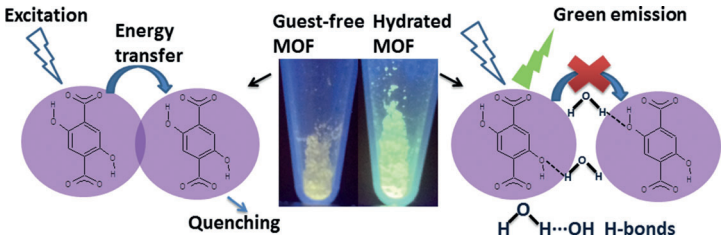


Scoped out: An efficient synthesis of the title compounds by a palladium-catalyzed C–H difluoroalkylation is described. This method features a broad substrate scope, operational simplicity, and utilizes readily available starting materials. BrettPhos was found to facilitate this transformation with unique efficiency. CPME = cyclopentyl methyl ether, dba = dibenzylidene acetone.

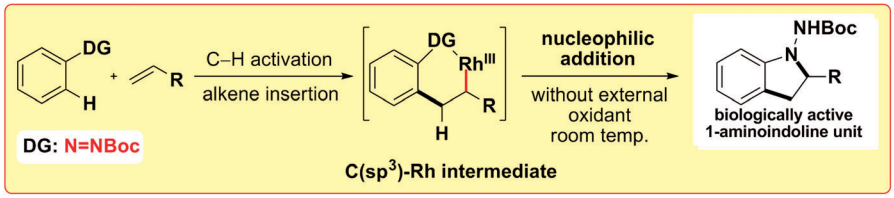
Microporous Materials

A. Douvali, A. C. Tsipis, S. V. Eliseeva,
S. Petoud, G. S. Papaefstathiou,
C. D. Malliakas, I. Papadas, G. S. Armatas,
I. Margiolaki, M. G. Kanatzidis,
T. Lazarides,* M. J. Manos* 1651 – 1656

Turn-On Luminescence Sensing and Real-Time Detection of Traces of Water in Organic Solvents by a Flexible Metal–Organic Framework



Testing the water: A Mg^{2+} metal–organic framework (MOF) is reported. It has the extraordinary capability to detect, in real time, trace water concentrations (0.05–5%) in various organic solvents through an unusual turn-on luminescence sensing mechanism. The sensitivity and fast response of this MOF for water, and its reusability, make it one of the most powerful water sensors known.



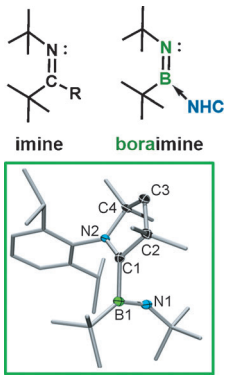
Buckle up! The nucleophilic addition of $C(sp^3)$–Rh species to polarized double bonds is the key step in a Rh^{III}-catalyzed C–H activation/cyclative capture reaction. This constitutes the first intermolecular catalytic method to directly access the 1-aminoindoline core with a broad substituent scope under mild conditions (Boc = *tert*-butoxycarbonyl, DG = directing group).

Heterocycles

D. Zhao, S. Vásquez-Céspedes, F. Glorius* ——— **1657 – 1661**

Rhodium(III)-Catalyzed Cyclative Capture Approach to Diverse 1-Aminoindoline Derivatives at Room Temperature

A B in C's clothing: The isolation and characterization of a set of carbene adducts of iminoboranes indicates diverse reactivity patterns. Simple adducts present "boraimine" structures, which mimic the organic imine functionality. Rearrangements of these simple adducts yield backbone-substituted carbenes as well as 1,2-azaborolidines.

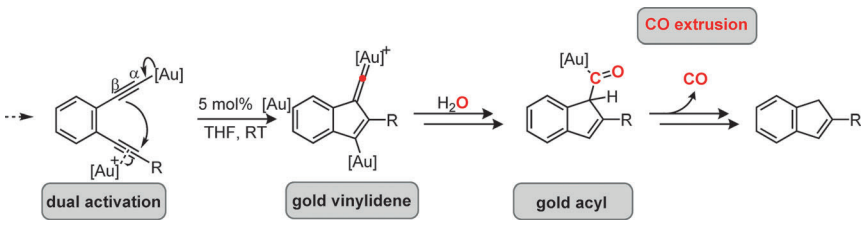


Iminoborane Adducts

H. Braunschweig,* W. C. Ewing, K. Geetharani, M. Schäfer ——— **1662 – 1665**

The Reactivities of Iminoboranes with Carbenes: BN Isosteres of Carbene–Alkyne Adducts

Inside Back Cover



Gold acyl intermediates are generated through the addition of water to gold vinylidene intermediates. The hitherto barely known gold acyl species are shown to undergo an extrusion of CO, an elementary step so far unknown in homogeneous gold catalysis. The reaction sequence constitutes a new gold-catalyzed decarbonylative indene synthesis.

Gold Catalysis

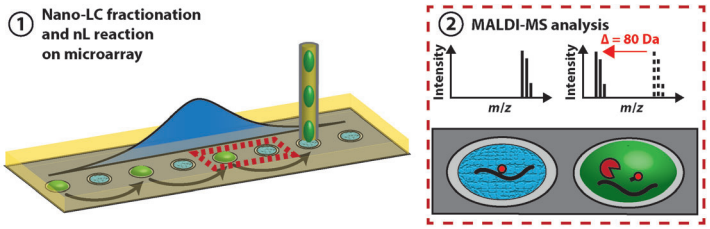
J. Bucher, T. Stößer, M. Rudolph, F. Rominger, A. S. K. Hashmi* ——— **1666 – 1670**

CO Extrusion in Homogeneous Gold Catalysis: Reactivity of Gold Acyl Species Generated through Water Addition to Gold Vinylidenes

Protein Phosporylation

S. K. Küster, M. Pabst,* R. Zenobi, P. S. Dittrich* ——— 1671 – 1675

Screening for Protein Phosphorylation Using Nanoscale Reactions on Microdroplet Arrays



Phosphopeptide screening: A mass spectrometry-based screening method detects protein phosphorylation in complex protein mixtures without extensive MS/MS experiments. The method employs droplet microfluidics to integrate nanoliter phosphatase reactions in a nano-LC-MALDI-MS workflow. The selective dephosphorylation of every second LC fraction induces characteristic peak fluctuations that can be used to identify even low-abundant phosphopeptides.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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