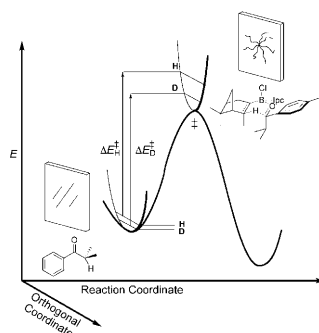


Broken mirrors: Kinetic isotope effects are excellent probes of transition structures. In this Concept, we describe recently developed kinetic isotope effect methodologies that serve to inform the symmetry-breaking process that is inherent to stereoselective reactions (see figure).

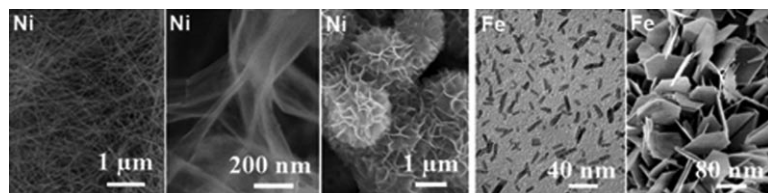


Reaction Mechanisms

*T. Giagou, M. P. Meyer** 10616–10628

Kinetic Isotope Effects in Asymmetric Reactions

COMMUNICATIONS



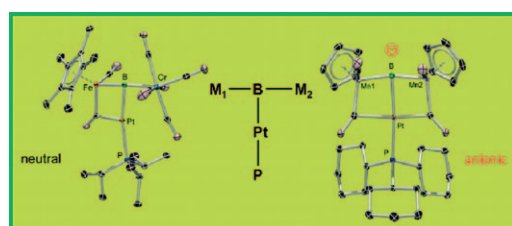
Galvanising chemistry! Galvanic replacement reactions have a very long history. However, its powerful capabilities have not been fully exploited for nanomaterial syntheses yet. Now, using very cheap, commercially available

Al/Mg powders as sacrificial materials, various metals (most transition and rare earth) with a large variety of novel nanostructures can be obtained easily on a very large scale (see picture).

Nanostructures

*G. Zhang, S. Sun, R. Li, X. Sun** 10630–10634

New Insight into the Conventional Replacement Reaction for the Large-Scale Synthesis of Various Metal Nanostructures and their Formation Mechanism



Time for T-shaped metalloborylenes: The first anionic trinuclear metal boron complex and a neutral analogue have been prepared and fully characterized. The unusual T-shaped geometry

renders the title compounds, transition-metal-base-stabilized metalloborylenes, which became available by an unprecedented direct synthetic approach.

Borylene Complexes

H. Braunschweig, K. Kraft, S. Östreicher, K. Radacki, F. Seeler* 10635–10637

Neutral and Anionic Transition-Metal-Base-Stabilized Metalloborylene Complexes

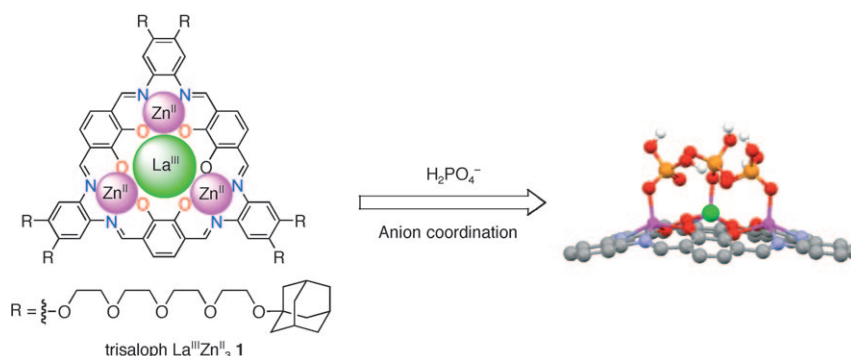


Self-Assembly

M. Yamamura, M. Sasaki, M. Kyotani,
H. Orita, T. Nabeshima* 10638–10643



Self-Assembled Nanostructures of Tailored Multi-Metal Complexes and Morphology Control by Counter-Anion Exchange



Improved solubility: Trisalophan complexes bearing PEGylated adamantane units were designed (see figure) and synthesized to improve their solubility in aqueous media. The complexes

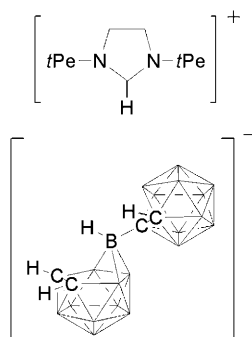
afforded a self-assembled nanostructure in aqueous media. Spherical and fibril aggregates were successfully formed based on the structural change caused by the coordinated anions.

Carboranes

C. E. Willans,* C. A. Kilner,
M. A. Fox* 10644–10648



Deboronation and Deprotonation of *ortho*-Carborane with N-Heterocyclic Carbenes



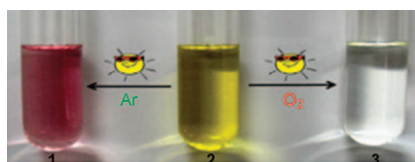
It is a matter of size: N-Heterocyclic carbenes can remove a proton from *ortho*-carborane to form a two-cage anion or attack the electropositive boron of *ortho*-carborane to yield a stable 1:2 carborane-carbene adduct. Which end product is formed depends on the steric bulk of the alkyl groups attached to the nitrogen atoms of the carbene.

Light Reactions

J. Bhuyan, S. Sarkar* 10649–10652



Oxidative Degradation of Zinc Porphyrin in Comparison with Its Iron Analogue



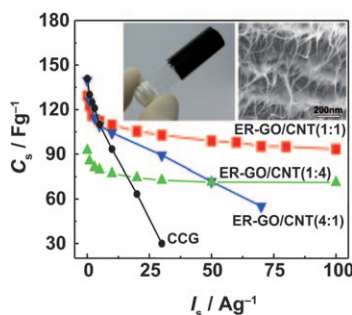
Solar conversion: Zinc hydroxyisoporphyrin (**2**), under sunlight and argon, is reduced back to zinc *meso*-tetraphenylporphyrin (**1**), but stays stable in oxygen in the absence of light. This behavior is in contrast to its iron analogue and stresses the redox role of iron in heme degradation. Compound **2** also responds to chlorophyll-type degradation (**3**) under sunlight and oxygen.

Carbon Nanotubes

L. Qiu, X. Yang, X. Gou, W. Yang,
Z.-F. Ma, G. G. Wallace,
D. Li* 10653–10658



Dispersing Carbon Nanotubes with Graphene Oxide in Water and Synergistic Effects between Graphene Derivatives



Synergistic graphenes: The chemical and electrical synergies between graphene derivatives enable a simple, cost-effective and environmentally friendly strategy for solution-phase processing of graphene oxide (GO) and carbon nanotubes (CNTs). The new nanohybrid exhibits high performance when used as electrodes for supercapacitors (see figure; ER = electrochemically reduced, CCG = chemically converted graphene).



En route to phosphinines: An efficient route to convert 1-phosphanorbornadienes into phosphinines is described (see scheme). This opens up the possi-

bility to use the broad and versatile phosphole chemistry as a starting point for an equally broad variety of phosphinines.

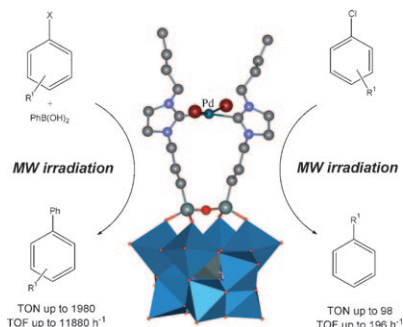
Phosphorus Chemistry

H. Wang, C. Li, D. Geng, H. Chen, Z. Duan,* F. Mathey* 10659–10661

A New Versatile Route for the Conversion of Phospholes into Phosphinines



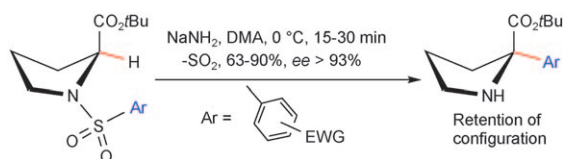
Better together: A novel hybrid N-heterocyclic carbene (NHC) palladium complex, integrating a totally inorganic and polyanionic decatungstate unit, has been synthesized following a convergent strategy. The interplay of the Pd binding domains with the inorganic scaffold is instrumental in accessing multi-turnover catalysis in C–C cross-coupling and aromatic dehalogenation reactions under MW-assisted protocols (see scheme).



Polyoxometalates

S. Berardi, M. Carraro, M. Iglesias, A. Sartorel, G. Scorrano, M. Albrecht,* M. Bonchio* 10662–10666

Polyoxometalate-Based N-Heterocyclic Carbene (NHC) Complexes for Palladium-Mediated C–C Coupling and Chloroaryl Dehalogenation Catalysis



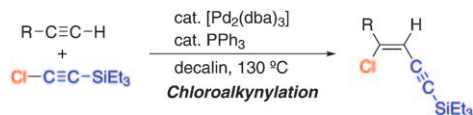
Enantiopure quaternary prolines have been prepared by stereoselective rearrangement of *N*-(arylsulfonyl)proline *tert*-butyl esters under basic conditions (see scheme), without any external source of stereochemical information. The sulfonamide aromatic ring must

contain an electron-withdrawing group (EWG), which stabilizes an intermediate Meisenheimer complex. The overall process provides easy entry to a series of optically pure α -aromatic prolines.

Enantioselective Rearrangements

F. Foschi, D. Landini, V. Lupi, V. Mihali, M. Penso,* T. Pilati, A. Tagliabue* 10667–10670

Enantioselective Rearrangement of Proline Sulfonamides: An Easy Entry to Enantiomerically Pure α -Aryl Quaternary Prolines



Useful intermediates: Addition of silyl-substituted chloroalkynes to terminal alkynes, namely chloroalkynylation, proceeds under palladium catalysis to afford (*Z*)-1-chloro-1,3-enynes (see scheme). The carbon–chlorine

bond of the adducts is easily convertible to a carbon–carbon bond by using palladium-catalyzed cross-coupling reactions to provide a variety of 1,3-enynes.

Palladium Catalysis

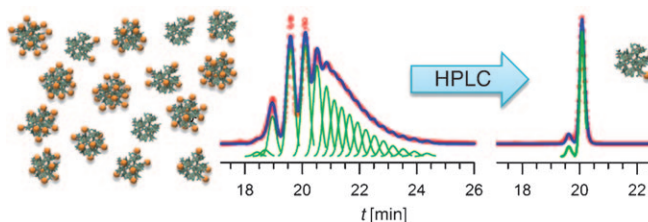
T. Wada, M. Iwasaki, A. Kondoh, H. Yorimitsu,* K. Oshima* 10671–10674

Palladium-Catalyzed Addition of Silyl-Substituted Chloroalkynes to Terminal Alkynes



Dendrimers

D. G. Mullen, E. L. Borgmeier,
A. M. Desai, M. A. van Dongen,
M. Barash, X.-m. Cheng,
J. R. Baker, Jr.,
M. M. Banaszak Holl* ... 10675–10678



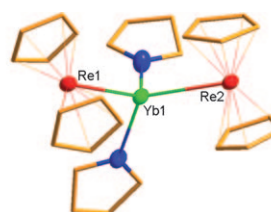
Isolation and Characterization of Dendrimers with Precise Numbers of Functional Groups

Precision dendrimer: Nine different dendrimer components with precise numbers of a functional ligand were

isolated leading to an order of magnitude improvement in the purity of each component.

Cluster Compounds

C. Döring, A.-M. Dietel,
M. V. Butovskii, V. Bezugly,
F. R. Wagner,*
R. Kempe* 10679–10683



Molecular [Yb(TM)₂] Intermetallics (TM = Ru, Re)

Salt of the (rare) earth: The reactions of ytterbium(II) iodide with alkali metal salts of the [CpRu(CO)₂] and [Cp₂Re] anions afford molecular compounds that have two unsupported

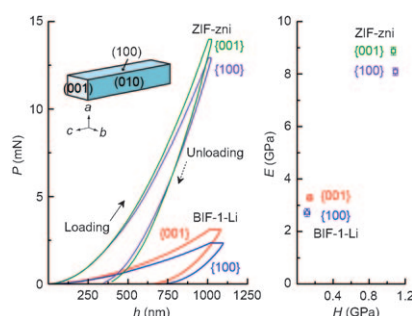
Yb–TM bonds (TM = transition metal; see scheme). Electron localisability indicator calculations were performed and revealed highly polar metal–metal bonds.

FULL PAPERS

Metal–Organic Frameworks

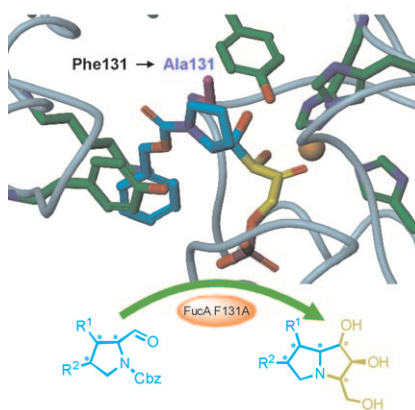
T. D. Bennett, J.-C. Tan,
S. A. Moggach, R. Galvelis,
C. Mellot-Draznieks, B. A. Reisner,
A. Thirumurugan, D. R. Allan,
A. K. Cheetham* 10684–10690

Mechanical Properties of Dense Zeolitic Imidazolate Frameworks (ZIFs): A High-Pressure X-ray Diffraction, Nanoindentation and Computational Study of the Zinc Framework Zn(Im)₂, and its Lithium–Boron Analogue, LiB(Im)₄



Dense ZIFs: Two topologically identical hybrid frameworks possess similar bulk moduli, yet strikingly different elastic moduli and hardnesses. The role of the inorganic species in each framework is scrutinised, with results drawn on the dominant factors involved in their mechanical response (see graphic). The results have far-reaching implications in the design of new hybrid materials, whilst explaining previous anomalies.

Minimal but hyper: One single mutation of FucA aldolase (F131A) extends its acceptor substrate tolerance to bulky and conformationally restricted *N*-Cbz-amino aldehydes (Cbz = benzyl-oxycarbonyl), including (*R*)-*N*-Cbz-prolinal, for which no detectable activity was observed with the FucA wild type. FucA F131A was an excellent catalyst for the aldol addition of dehydroxyacetone phosphate to hydroxyprolinal derivatives (see figure), leading to novel polyhydroxylated pyrrolizidines related to the hyacinthacine and alexine types.

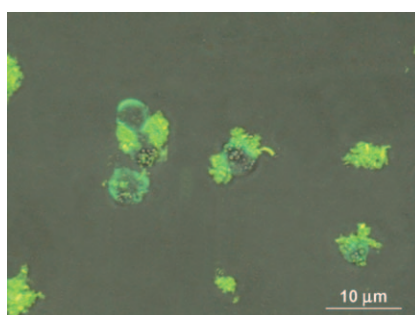


Enzyme Modification

X. Garrabou, L. Gómez, J. Joglar, S. Gil, T. Parella, J. Bujons, P. Clapés** 10691 – 10706

Structure-Guided Minimalist Redesign of the L-Fucose-1-Phosphate Aldolase Active Site: Expedient Synthesis of Novel Polyhydroxylated Pyrrolizidines and their Inhibitory Properties Against Glycosidases and Intestinal Disaccharidases

Cancer measures up: Electrochemical and electrochemiluminescence cytosensors for the detection of Ramos cells has been developed by taking advantage of the easy separation of magnetic beads and the high affinity of aptamers with and without amplification of the nanoparticles (see figure).

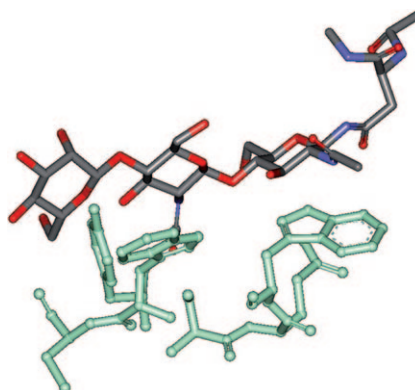


Electrochemistry

*C. Ding, Y. Ge, S. Zhang** 10707 – 10714

Electrochemical and Electrochemiluminescence Determination of Cancer Cells Based on Aptamers and Magnetic Beads

Sugar recognition and allergies: A combined approach of NMR spectroscopy and molecular modeling (see figure) has permitted us to deduce the structure of Asn-linked Man(GlcNAc)₂ bound to hevein. Given the ubiquity of the Man(GlcNAc)₂ core in all mammalian *N*-glycoproteins, the basic recognition mode presented herein might be extended to a variety of systems with biomedical importance.

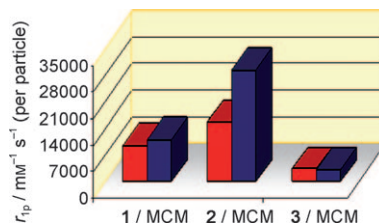


Amino Acid Synthesis

J. J. Hernández-Gay, A. Ardá, S. Eller, S. Mezzato, B. R. Leeftang, C. Unverzagt, F. J. Cañada, J. Jiménez-Barbero** 10715 – 10726

Insights into the Dynamics and Molecular Recognition Features of Glycopeptides by Protein Receptors: The 3D Solution Structure of Hevein Bound to the Trisaccharide Core of *N*-Glycoproteins

Just relax! Three different Gd^{III} complexes were anchored on the surface of MCM-41 silica nanoparticles functionalised with –NH₂ groups. The porous support markedly influences the magnetic properties of the Gd^{III} chelates. The dramatic relaxivity enhancement observed after acetylation of the amino groups (see figure) results in an extremely high magnetic resonance imaging (MRI) sensitivity per particle.



Molecular Imaging

F. Carniato, L. Tei, M. Cossi, L. Marchese, M. Botta** 10727 – 10734

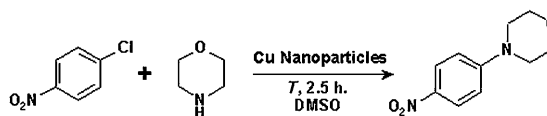
A Chemical Strategy for the Relaxivity Enhancement of Gd^{III} Chelates Anchored on Mesoporous Silica Nanoparticles

Nanoparticles

Y. Wang, A. V. Biradar, G. Wang,
K. K. Sharma, C. T. Duncan,
S. Rangan, T. Asefa* 10735–10743

Controlled Synthesis of Water-Dispersible Faceted Crystalline Copper Nanoparticles and Their Catalytic Properties

Control the shape: Copper nanoparticles with tunable sizes and shapes were synthesized by reducing copper(II) salt with hydrazine in an aqueous solution that contained poly(acrylic acid) (PAA) as the capping agent. Cubocta-

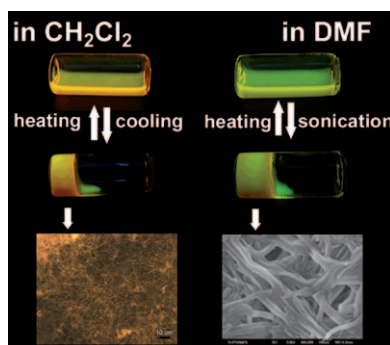


hedron-shaped copper nanoparticles were readily obtained by adjusting the concentration of PAA. Among other applications, they have shown significant catalytic activity and selectivity in C–N coupling (see scheme).

Supramolecular Assembly

C. Dou, C. Wang, H. Zhang,* H. Gao,
Y. Wang* 10744–10751

Novel Urea-Functionalized Quinacridone Derivatives: Ultrasound and Thermo Effects on Supramolecular Organogels

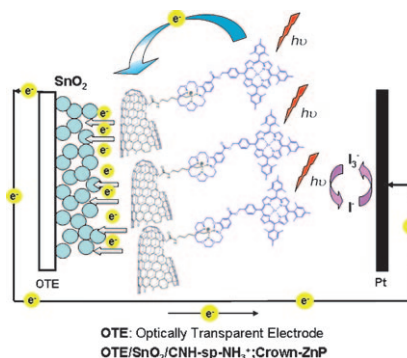


Instant gel: Two novel urea-functionalized quinacridone derivatives have been designed and synthesized, and multi-stimuli-responsive organogels based on these smart materials have been obtained. Environmental factors, such as temperature and sonication, can effectively tune their supramolecular assembly properties (see figure) and provide a deep understanding of the mechanism of stimuli-responsive gelation.

Nanomaterials

M. Vizuite, M. J. Gómez-Escalonilla,
J. L. G. Fierro, A. S. D. Sandanayaka,
T. Hasobe,* M. Yudasaka,* S. Iijima,
O. Ito,* F. Langa* 10752–10763

A Carbon Nanohorn–Porphyrin Supramolecular Assembly for Photoinduced Electron-Transfer Processes

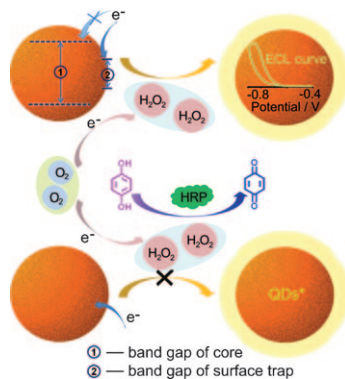


Around the horn: A new light-sensitive nanohybrid based on a carbon nanohorn (CNH) and a zinc-porphyrin bearing a crown ether group (CNH-sp-NH₃⁺; Crown-ZnP) has been prepared by a relatively simple self-assembly procedure. Photoinduced electron-transfer processes of the nanohybrids are confirmed, and the moderate efficiency of this system in photovoltaic solar cells is shown.

Quantum Dots

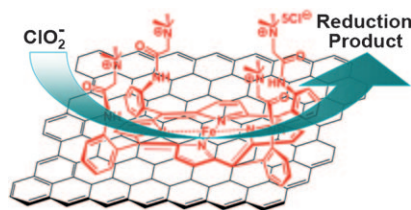
X. Liu, L. Cheng, J.-P. Lei, H. Liu,
H.-X. Ju* 10764–10770

Formation of Surface Traps on Quantum Dots by Bidentate Chelation and Their Application in Low-Potential Electrochemiluminescent Biosensing



A narrow surface band gap and low-potential electrochemiluminescence (ECL) of quantum dots (QDs) were achieved by using dithiol compound as a stabilizer to form surface traps on the QDs. H₂O₂ produced from the reduction of dissolved oxygen was demonstrated to be the co-reactant of the cathodic ECL process, which could lead to the extensive application of the QDs in ECL biosensing for peroxidase-related analytes.

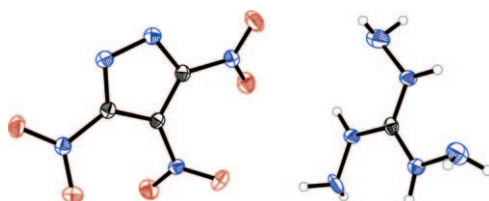
Unseen power of the picket fence: A biofunctional nanocomposite of reduced graphene oxide (RGO) with water-soluble picket-fence iron porphyrin (FeTMAPP) has been prepared through π - π interactions (see image). It has good biocompatibility and dispersion in water, and shows fast electronic communication between the porphyrin plane and flattened RGO for chlorite reduction.



Porphyrinoids

W. Tu, J. Lei,* S. Zhang,
H. Ju* 10771–10777

Characterization, Direct Electrochemistry, and Amperometric Biosensing of Graphene by Noncovalent Functionalization with Picket-Fence Porphyrin



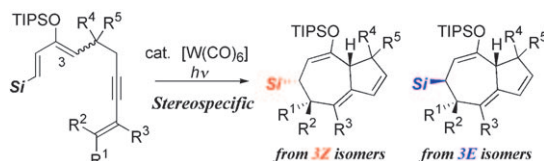
Out with a bang! From the calculated detonation pressure (23.74–31.89 GPa) and velocity (7586–8543 ms⁻¹), 3,4,5-trinitropyrazolate salts have potential as energetic materials. Impact sensitivity

ties were determined to be no less than 35 J by hammer tests, which placed these salts in the insensitive class.

Explosives

Y. Zhang, Y. Guo, Y.-H. Joo,
D. A. Parrish,
J. M. Shreeve* 10778–10784

3,4,5-Trinitropyrazole-Based Energetic Salts



Tungsten-catalyzed tandem cyclization of 3-siloxy-1,3,9-triene-7-yne derivatives allowed stereoselective preparation of a variety of synthetically useful functionalized bicyclo[5.3.0]decane derivatives (see scheme). This reaction

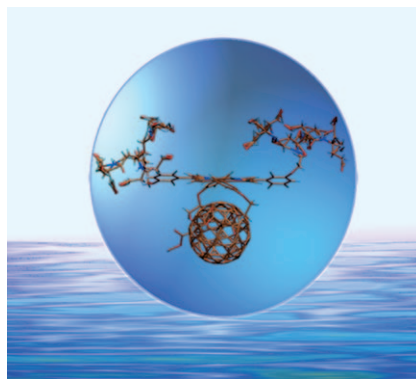
should provide a powerful method for the synthesis of natural products with a bicyclo[5.3.0]decane framework from easily available acyclic precursors. **Si** = Me₂PhSi, TIPS = *i*Pr₃Si.

Synthetic Methods

Y. Onizawa, M. Hara, T. Hashimoto,
H. Kusama,
N. Iwasawa* 10785–10796

Synthetic Studies on and Mechanistic Insight into [W(CO)₅(L)]-Catalyzed Stereoselective Construction of Functionalized Bicyclo[5.3.0]decane Frameworks

Fullerenes: A series of truly water-soluble and tightly coupled porphyrin/C₆₀ electron-donor-acceptor conjugates (see figure) have been synthesized, in which the charge-separation and charge-recombination dynamics are controlled by modifying the nature of the dendrimer and/or the choice of the central metal atom.



Charge Transfer

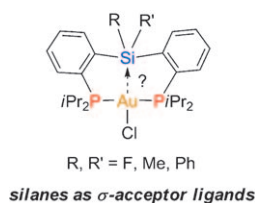
M. Ruppert, F. Spänig, M. Wielopolski,
C. M. Jäger, W. Bauer, T. Clark,*
A. Hirsch,*
D. M. Guldi* 10797–10807

Dendronizing and Metalating *trans*-2 C₆₀ Tetraaryl Porphyrins—A Versatile Approach Toward Water-Soluble Donor-Acceptor Conjugates

Sigma-Acceptor Ligands

P. Gualco, M. Mercy, S. Ladeira,
Y. Coppel, L. Maron,* A. Amgoune,*
D. Bourissou* 10808–10817

Hypervalent Silicon Compounds by Coordination of Diphosphine–Silanes to Gold

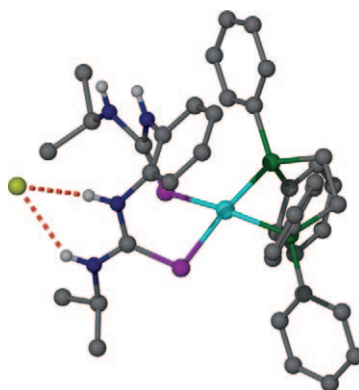


Metal→silane interactions: Coordination of ambiphilic diphosphine–silane ligands $o-[(iPr_2P)C_6H_4]_2SiRR'$ to AuCl affords pentacoordinate neutral silicon compounds in which the metal center acts as a two-electron donor and the silane as a σ -acceptor ligand (see picture). Spectroscopic, structural, and theoretical data substantiate the influence of the substitution pattern at silicon on the Au→Si interaction.

Organometallic Anion Hosts

M. L. Soriano, J. T. Lenthall,
K. M. Anderson, S. J. Smith,
J. W. Steed* 10818–10831

Enhanced Anion Binding from Unusual Coordination Modes of Bis-(thiourea) Ligands in Platinum Group Metal Complexes

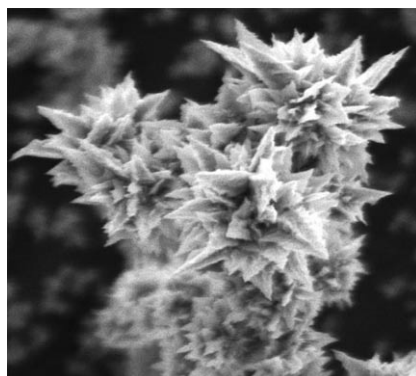


Unusual bindings: Treatment of a range of bis(thiourea) ligands with inert organometallic transition-metal ions gives a number of novel complexes that exhibit unusual ligand binding modes and significantly enhanced anion binding ability.

Pt SALDI Substrates

H. Kawasaki,* T. Yao, T. Suganuma,
K. Okumura, Y. Iwaki, T. Yonezawa,
T. Kikuchi, R. Arakawa* 10832–10843

Platinum Nanoflowers on Scratched Silicon by Galvanic Displacement for an Effective SALDI Substrate

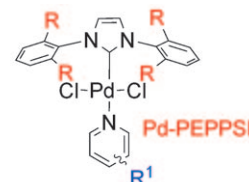


Platinum nanoflowers: We report a new and facile method for synthesizing three-dimensional (3D) platinum nanoflowers (Pt Nfs) on a scratched silicon substrate by electroless galvanic displacement (see SEM image). The Pt Nf silicon hybrid plate shows excellent surface-assisted laser desorption/ionization (SALDI) activity.

Catalyst Activation

J. Nasielski, N. Hadei, G. Achonduh,
E. A. B. Kantchev, C. J. O'Brien,
A. Lough, M. G. Organ* 10844–10853

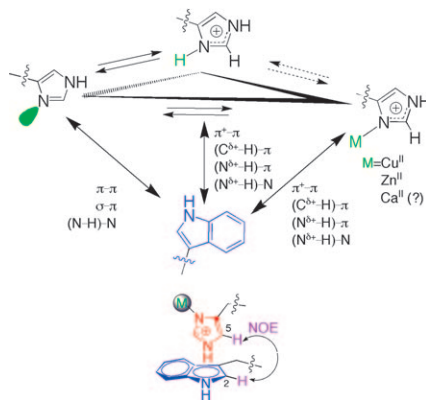
Structure–Activity Relationship Analysis of Pd–PEPPSI Complexes in Cross-Couplings: A Close Inspection of the Catalytic Cycle and the Precatalyst Activation Model



Get active! An array of N-heterocyclic carbene and pyridine ligands were evaluated in a wide variety of coupling reactions to probe the activation of the

Pd–PEPPSI (pyridine, enhanced, pre-catalyst, preparation, stabilisation and initiation) catalyst (see scheme).

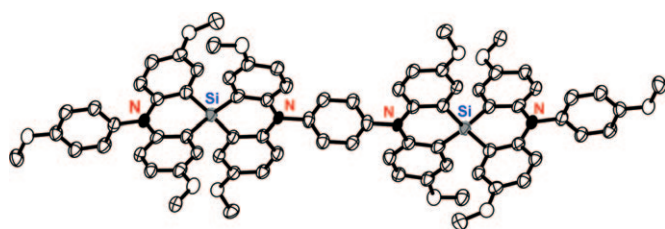
A sense of direction: Perturbed Trp side-chain structure heterogeneity due to putative π interactions allowed us to use ^{13}C NMR spectroscopy and NOESY to investigate Trp rotamer conformations near metal-binding centers. The observed C–H2(indolyl)–C–H5(Im $^+$) connectivity suggests that the N–H 1 of the Ca $^{2+}$ –Im $^+$ unit interacts with the pyrrole ring of the indole moiety in the Ca $^{2+}$ -bound scaffold, which is assignable to a moderately static, T-shaped, interplanar $\pi^+-\pi$ stacking alignment (see scheme).



Pi Bonding

C. M. Yang,* J. Zhang ... 10854–10865

Insights into Intramolecular Trp and His Side-Chain Orientation and Stereospecific π Interactions Surrounding Metal Centers: An Investigation Using Protein Metal-Site Mimicry in Solution



Redox diversity: A *para*-phenylene-bridged spirobi(triarylamine) dimer (see graphic), in which π conjugation through four redox-active triarylamine subunits is partially segregated by the unique perpendicular conformation, is

characterized by structural, electrochemical, and spectroscopic methods. The electronic structures of the radical cation, dication, and oxidized species are established.

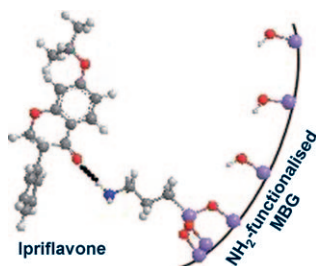
Spiro Compounds

A. Ito,* K. Hata, K. Kawamoto, Y. Hirao, K. Tanaka, M. Shiro, K. Furukawa, T. Kato 10866–10878

***para*-Phenylene-Bridged Spirobi(triarylamine) Dimer with Four Perpendicularly Linked Redox-Active π Systems**



Bone machine: Mesoporous bioactive glasses (MBGs) have been functionalised to achieve long-term delivery of an anti-osteoporotic drug (see graphic), thereby opening the possibility for it to remain until the formation of new tissue. Combined with the extraordinary bioactivity of MBGs, these materials would be excellent candidates for use in bone-tissue regeneration.



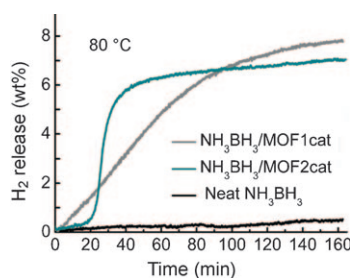
Drug Delivery

A. López-Noriega, D. Arcos, M. Vallet-Regí* 10879–10886

Functionalizing Mesoporous Bioglasses for Long-Term Anti-Osteoporotic Drug Delivery



Hold and release: Two novel catalysts, synthesized from metal–organic frameworks (MOFs), significantly lower the reaction onset temperature and accelerate the release of H $_2$ from ammonium borane during the thermal decomposition process at $\leq 90^\circ$ (see figure). The in situ generated Ni 0 and the MOF structure of the MOF-based catalysts are proven to present significant and different effects in promoting catalytic activities.



Materials Science

Y. Li, P. Song, J. Zheng, X. Li* 10887–10892

Promoted H $_2$ Generation from NH $_3$ BH $_3$ Thermal Dehydrogenation Catalyzed by Metal–Organic Framework Based Catalysts



* Author to whom correspondence should be addressed



Supporting information on the WWW (see article for access details).



Full Papers labeled with this symbol have been judged by two referees as being "very important papers".



A video clip is available as Supporting Information on the WWW (see article for access details).

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CORRIGENDUM

*K. Ahlford, J. Ekström, A. B. Zaïzsev,
P. Ryberg, L. Eriksson,
H. Adolfsson** 11197–11209

**Asymmetric Transfer Hydrogenation
of Ketones Catalyzed by Amino Acid
Derived Rhodium Complexes: On the
Origin of Enantioselectivity and Enan-
tioswitchability**

Chem. Eur. J., **2009**, *15*

DOI: 10.1002/chem.200900548

In their Full Paper, the authors have found that the CCDC number in reference [17], which contains crystallographic data of the rhodium complex presented in Figure 2, is unfortunately incorrect. The correct CCDC number is 736138 and not 712178. The authors sincerely apologize for this error and any inconvenience it may have caused.

