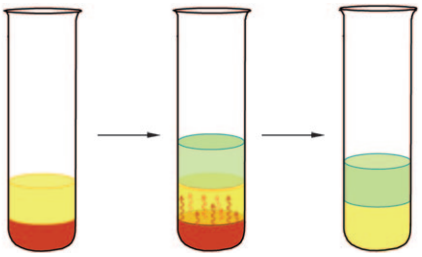
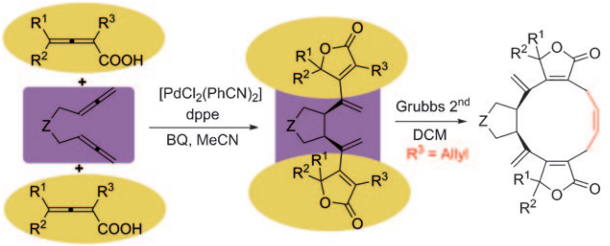
CONCEPTS

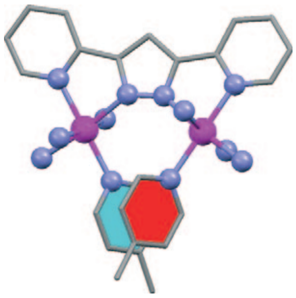


Now you see it, now you don't! Phase-vanishing reactions utilize a perfluorinated solvent as a liquid membrane to separate a substrate and a reagent (see figure; yellow = perfluorinated solvent, red = reagent, green = substrate). A variety of experimental designs allows for reactions to be carried out under anhydrous conditions, under photolytic conditions, under solvent-free conditions, with a gas as a reagent, and under reflux.

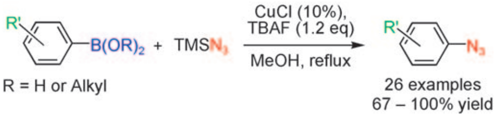
COMMUNICATIONS



Triple-decker sandwich: A sandwich-type triple cyclization of two molecules of 2,3-allenoic acid and one molecule of 1,5-bisallene in the presence of a palladium catalyst with excellent stereoselectivity has been developed. The diallyl-substituted *cis* products may easily be transformed to fused tetracyclic compounds with a 12-membered ring (see scheme). Based on the result of optically active 2,3-allenoic acids, a possible catalytic cycle has been proposed.



Molecular twisting: A family of dinuclear Ru complexes of general formula $[\{Ru(T)(L)\}_2(\mu\text{-bpp})]^{(n+1)+}$ (T = tridentate meridional ligand; bpp = tetradentate bridging ligand and L = monodentate ligand, $n = 1$ or 2) have been prepared and thoroughly characterized. In solution these complexes display a global dynamic behavior in which the monodentate ligands undergo a synchronized twisting motion.

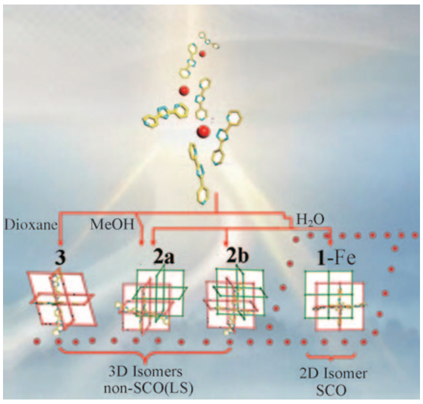


Aryl azide formation: The copper-catalyzed coupling reaction of boronic esters and acids with TMSN$_3$ have been presented as a highly efficient, simple, broadly applicable, and less hazardous methodology for the practical synthesis of aryl azides with structural diversity (see scheme).

Bistable Materials

X. Bao, J.-L. Liu, J.-D. Leng, Z. Lin, M.-L. Tong, M. Nihei, H. Oshio* .... 7973 – 7978

Spin Crossover versus Low-Spin Behaviour Exhibited in 2D and 3D Supramolecular Isomers of $[Fe^{II}(2,4\text{-}bpt)_2]\cdot$Guest

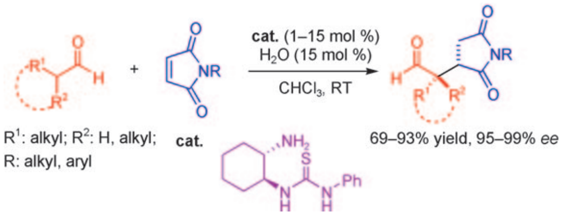


To spin or not to spin: Four supramolecular isomers based on a $[Fe(2,4\text{-}bpt)_2]\cdot$guest were synthesised by judicious choice of solvents under solvothermal conditions (see figure). They can be categorised into a 2D spin crossover (SCO) branch and a 3D low-spin (LS) branch (all of them exhibit NbO topology, but one is non-interpenetrated and the other two are twofold interpenetrated). The differences in the supramolecular interactions play important roles in their magnetic behaviour.

Organocatalysis

F. Xue, L. Liu, S. Zhang, W. Duan, W. Wang** .... 7979 – 7982

A Simple Primary Amine Thiourea Catalyzed Highly Enantioselective Conjugate Addition of α,α-Disubstituted Aldehydes to Maleimides

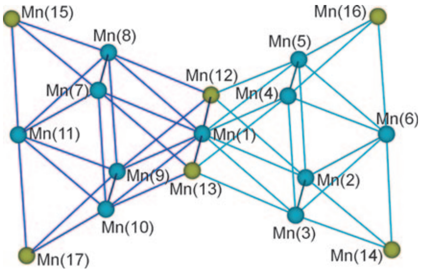


Branch point: A simple primary amine thiourea catalyzed highly enantioselective conjugate addition of α,α-disubstituted aldehydes to maleimides has been developed. The biologically useful chiral disubstituted α-branched succinimides are attained with the generation of two contiguous quaternary and/or tertiary stereogenic centers in one step with excellent enantioselectivities and in high yields under mild reaction conditions (see scheme).

Coordination Chemistry

G. E. Kostakis, A. K. Powell* .... 7983 – 7987

Coordination Chemistry Without Frontiers: A Short Analysis and Applications of a New Method for the Description of Closed Coordination Clusters

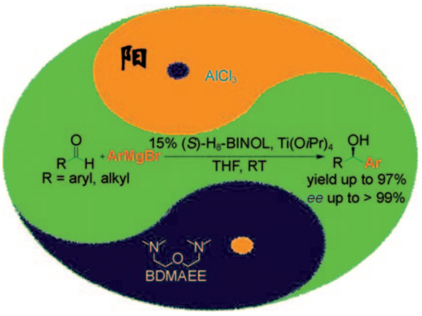


Understanding nucleation: An approach for describing the topology of coordination clusters illustrated by some examples (see graphic) that are helpful in understanding nuclear growth (nucleation) is presented.

Asymmetric Synthesis

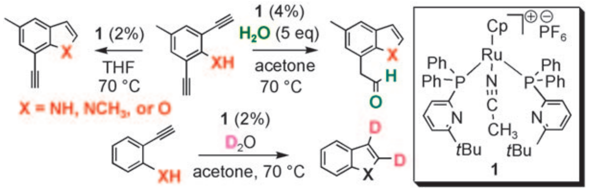
*X.-Y. Fan, Y.-X. Yang, F.-F. Zhuo, S.-L. Yu, X. Li, Q.-P. Guo, Z.-X. Du, C.-S. Da** .... 7988 – 7991

$AlCl_3$ and BDMAEE: A Pair of Potent Reactive Regulators of Aryl Grignard Reagents and Highly Catalytic Asymmetric Arylation of Aldehydes



Cheap, energy-saving, and applicable: With the aid of $AlCl_3$ and BDMAEE [2,2′-oxybis(*N*,*N*-dimethylethanamine)], a highly asymmetric catalytic addition of various aryl Grignard reagents to aldehydes was achieved under mild conditions with easily prepared (*S*)-H_8-BINOL and inexpensive commercially available $Ti(O\mathit{i}Pr)_4$ (see scheme), and the reaction could be easily scaled up with no loss of yield and enantioselectivity.

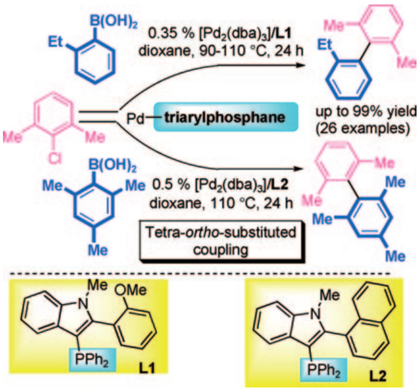
Metal Vinylidenes



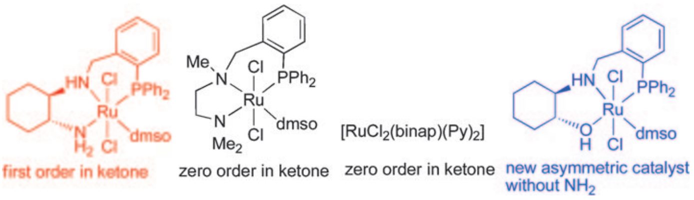
Bifunctional is more than twice as fun! At low loading, catalyst **1** (see scheme) can form two important heterocycle classes, apparently by attack of XH on a vinylidene intermediate. Aza- and nitroindoles can be formed, and all *N*-protecting groups tested (alkyl, allyl, sulfonyl) were tolerated. The newly formed ring can be deuterated in one step, and for substrates with two terminal alkynes, cyclization can be followed by hydration, making this catalyst uniquely versatile.

Cross-Coupling Reactions

Expanding the horizons of $ArPPh_2$: New applications of triarylphosphane ligands are presented. The Pd–**L1** and Pd–**L2** complexes offer exceptionally high activity in Suzuki–Miyaura cross-couplings of aryl chlorides. The extremely congested synthesis of tetra-*ortho*-substituted biaryl compounds is achieved for the first time by simply using triarylphosphane ligands.



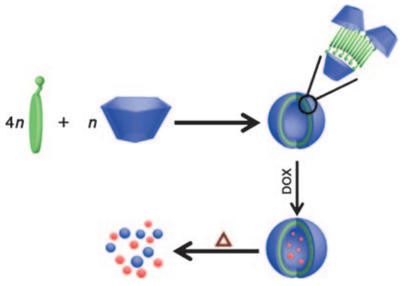
Asymmetric Hydrogenation



Redesign and reduce: The graphic shows some Ru complexes of tridentate ligands that do not contain NH substituents but can catalyse ketone reduction with zero-order dependence on ketone. In tridentate systems, a secondary amine, not a primary amine, promotes hydrogen activation. Leading on from these observations, the Ru complex of a phosphine-amino-alcohol shown above has been found to be a good hydrogenation catalyst.

Host–Guest Systems

Supramolecular vesicles were successfully constructed on the basis of host–guest complex formation between *p*-sulfonatocalix[5]arene and 1-pyrenemethylaminium. The obtained vesicles exhibit benign water solubility, self-labeled fluorescence, and more importantly, temperature-response characteristics; these features mean that the vesicles can act as potential delivery models for special substrates (see figure; DOX = doxorubicin hydrochloride).

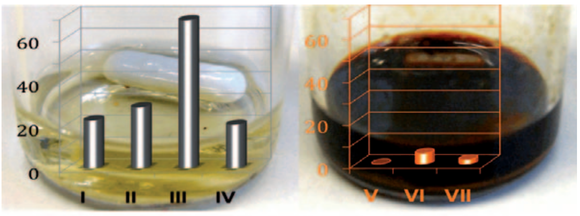


FULL PAPERS

Homogeneous Catalysis

A. S. K. Hashmi, C. Lothschütz, M. Ackermann, R. Doepp, S. Anantharaman, B. Marchetti, H. Bertagnolli,* F. Rominger* .... 8012 – 8019

Gold Catalysis: In Situ EXAFS Study of Homogeneous Oxidative Esterification

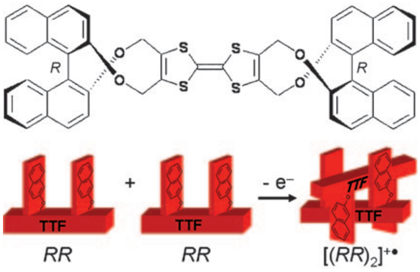


All that glitters! Investigations into gold-catalysed oxidative esterification with gold–pyridine complexes proves that the oxidation is truly homogeneous. The reaction flasks after the reaction has taken place under stabilised conditions (**I–IV**) and non-stabilised conditions (**V–VII**) are depicted.

Electrochemistry

*A. Saad, F. Barrière, E. Levillain, N. Vanthuyne, O. Jeannin, M. Fourmigué** .... 8020 – 8028

Persistent Mixed-Valence $[(\mathrm{TTF})_2]^{+\bullet}$ Dyad of a Chiral Bis(binaphthol)–tetrathiafulvalene (TTF) Derivative

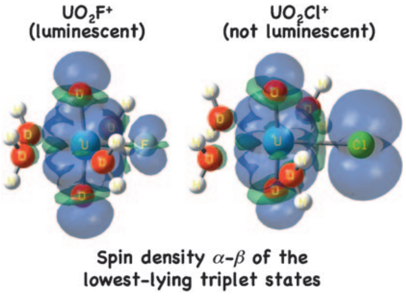


Mixed with a clip: Enantiomers of a chiral bis(binaphthol)tetrathiafulvalene derivative self-associate upon oxidation into a rare and persistent mixed-valence $[(\mathrm{TTF})_2]^{+\bullet}$ (TTF = tetrathiafulvalene) dyad through an unprecedented non-covalent clip (see image). Only the *RR* and *SS* enantiomers can form the dyad, which is not observed with the *meso* derivative.

Photochemistry

S. Tsushima, C. Götz, K. Fahmy* .... 8029 – 8033

Photoluminescence of Uranium(VI): Quenching Mechanism and Role of Uranium(V)

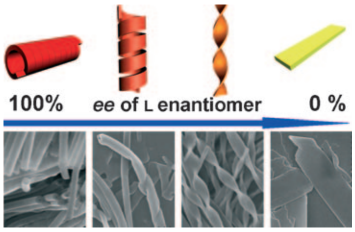


The luminous character of U! The structures and spin density $\alpha-\beta$ of the lowest-lying triplet states of uranyl(VI) halides show the origins of the electronic transitions and represent the luminescence characters of these complexes (see graphic).

Organogels

*X. Zhu, Y. Li, P. Duan, M. Liu** .... 8034 – 8040

Self-Assembled Ultralong Chiral Nanotubes and Tuning of Their Chirality Through the Mixing of Enantiomeric Components

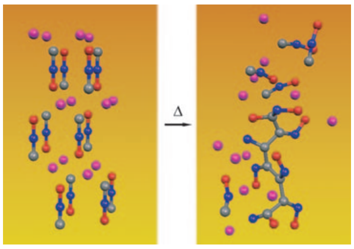


Starting to gel: Enantiomeric L- or D-glutamic acid based lipids were found to form an organogel composed of ultralong chiral nanotubes in ethanol. Mixing the enantiomers in different ratios caused the nanotubes to change into nanotubes with a helical seam, then nanotwists, and then nanosheets (see figure) with tunable chirality.

Molecular Dynamics

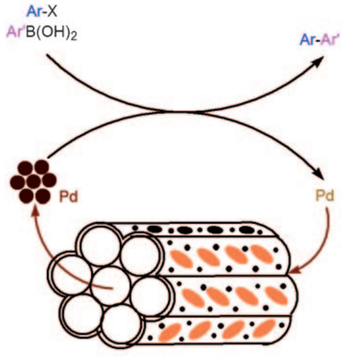
*K. Damianos, I. Frank** .... 8041 – 8046

Car–Parrinello Molecular Dynamics Study of the Thermal Decomposition of Sodium Fulminate



Fulminating: The high-temperature decomposition of sodium fulminate is simulated by using Car–Parrinello molecular dynamics. Rapid formation of carbon–carbon bonds led to polymerisation. The reaction mechanism explains why fulminates behave differently from the isoelectronic azides.

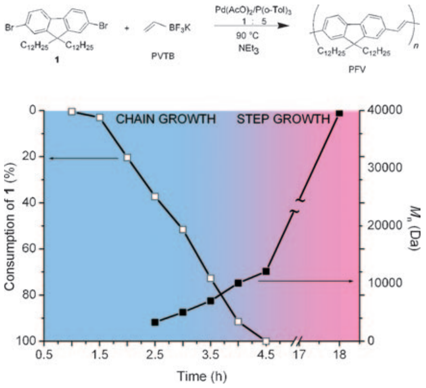
Support chemistry! We have demonstrated that a Pd-supported periodic mesoporous organosilica ionic liquid (Pd@PMO-IL **1**) is an efficient and reusable catalyst for the Suzuki–Miyaura coupling reaction of even deactivated aryl chlorides in water (see scheme). The catalyst can be recovered and reused for at least four reaction cycles without significant loss of activity.



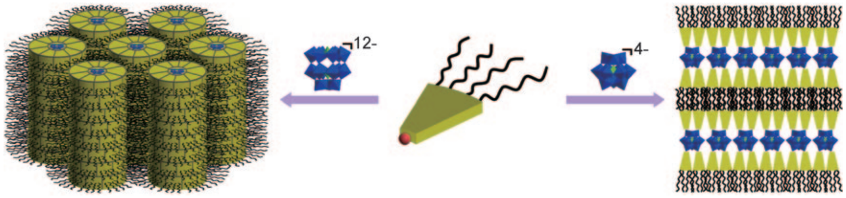
Pd@PMO-IL **1**

Ionic Liquids

Chain growth versus step growth: The first example of a metal-catalysed polycondensation reaction to obtain poly(arylene vinylene)s through a chain-growth mechanism followed by a step-growth process is presented (see figure).



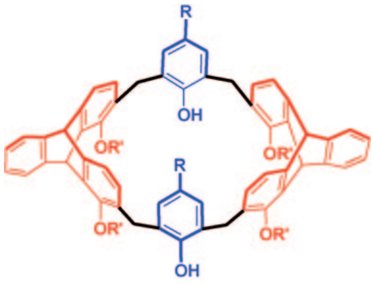
Polycondensation Reactions



Structural controlling: Dendritic surfactant-encapsulated polyoxometalate complexes with different numbers of dendrons have been prepared. On increasing the number of dendrons, the complex dendrimers change from globular assembled states to monodispersions in solution and from lamellar to hexagonal columnar structures in the solid state (see graphic).

Self-Assembly

Rigidified calixarene hosts: A series of novel triptycene-derived calix[6]arenes (shown here) have been efficiently synthesized. Structural studies revealed that all of the macrocycles have well-defined structures with fixed conformations both in solution and in the solid state owing to the introduction of the triptycene moiety with a rigid three-dimensional structure.



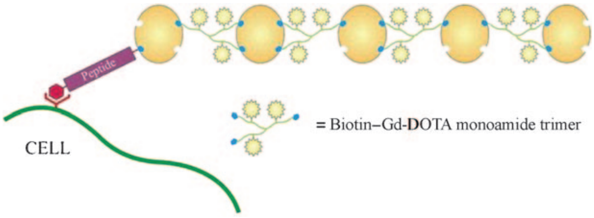
R=H, *t*Bu, Ph; R' = H, Me

Host–Guest Systems

Magnetic Resonance Imaging

*L. Tei, A. Barge, S. Geninatti Crich, R. Pagliarin, V. Negri, D. Ramella, G. Cravotto, S. Aime** 8080–8087

Target Visualization by MRI Using the Avidin/Biotin Amplification Route: Synthesis and Testing of a Biotin–Gd-DOTA Monoamide Trimer

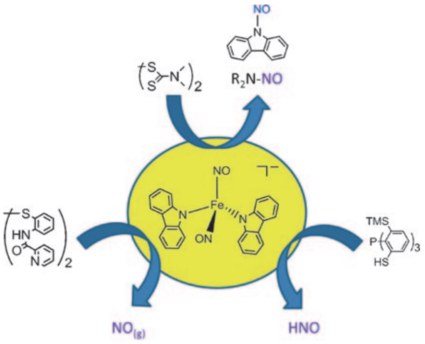


Super supramolecular adducts! Biotin–Gd-DOTA monoamide trimers able to form very large (MW > 2 MDa) supramolecular adducts with (strept)avidin were synthesized. One of these systems, endowed with high relaxivity, allowed the MRI visualization of Kaposi's sarcoma cells and tumor endothelial cells (see scheme; DOTA = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid).

Bioinorganic Chemistry

*T.-T. Lu, C.-H. Chen, W.-F. Liaw** 8088–8095

Formation of the Distinct Redox-Interrelated Forms of Nitric Oxide from Reaction of Dinitrosyl Iron Complexes (DNICs) and Substitution Ligands

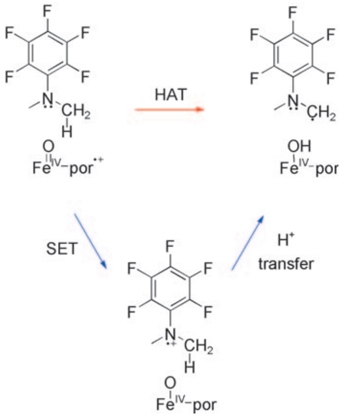


Accept NO substitute! Incoming substitution ligands play a key role in modulating the generation of the distinct redox-interrelated forms of NO (*N*-nitrosocarbazole, ˙NO, and HNO/NO^-) derived from reactions of the dinitrosyl iron complex $[(NO)_2Fe(C_{12}H_8N)_2]^-$ and ligands $(S_2CNMe_2)_2$, $(PyPepS)_2$, and $P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}SH)_3$, respectively (see scheme).

Reaction Mechanisms

*K. M. Roberts, J. P. Jones** 8096–8107

Anilinic N-Oxides Support Cytochrome P450-Mediated N-Dealkylation through Hydrogen-Atom Transfer

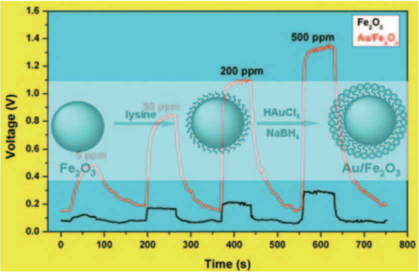


You can SET your HAT on: 2,3,4,5,6-Pentafluoro-*N*,*N*-dimethylaniline *N*-oxide was tested in cytochrome P450cam and found to support the N-dealkylation of two distinct tertiary anilines. Product formation as well as kinetic and theoretical arguments exclude a single-electron-transfer (SET) mechanism for N-dealkylation in favor of hydrogen-atom transfer (HAT; see scheme, por = porphyrin).

Hybrid Materials

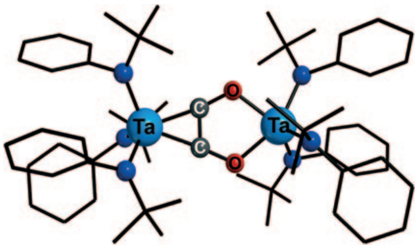
*J. Zhang, X. Liu, X. Guo, S. Wu, S. Wang** 8108–8116

A General Approach to Fabricate Diverse Noble-Metal (Au, Pt, Ag, Pt/Au)/Fe_2O_3 Hybrid Nanomaterials



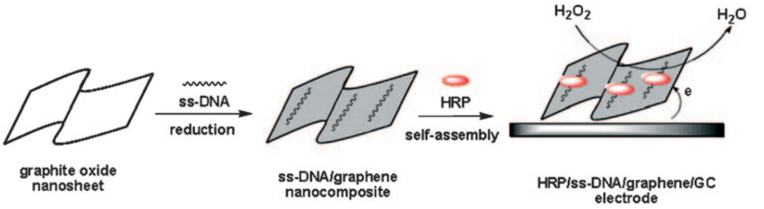
Dual control! A novel, facile, and general one-pot strategy is explored for constructing diverse noble-metal (Au, Pt, Ag or Pt/Au)/Fe_2O_3 hybrid nanoparticles by using lysine as a dual linker and capping reagent (see figure). The hybrid Au/Fe_2O_3 nanoparticles exhibit significantly improved sensor performance in terms of high sensitivity, low detection limit, good selectivity, and reproducibility in comparison to pristine Fe_2O_3.

Reaction Mechanisms



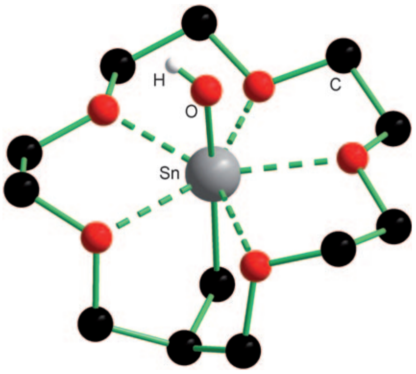
The experimentally known reduction of carbon monoxide by using a 3-coordinate [Ta(silox)$_3$] (silox = OSi(*t*Bu)$_3$) complex initially forms a ketenylidene [(silox)$_3$Ta–CCO], followed by a dicarbide [(silox)$_3$Ta–CC–(silox)$_3$] structure. The mechanism for this intricate reaction has finally been revealed by using density functional theory, and importantly a likely structure for the previously unknown intermediate [(silox)$_3$Ta–CO]$_2$ has been identified (see figure).

Biosensors



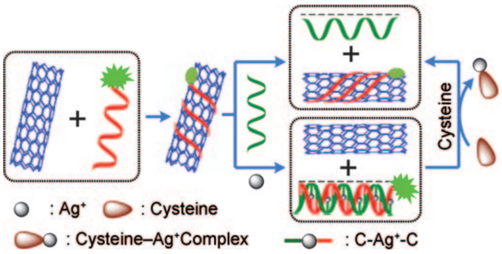
Enzyme in an electrode: As a biocompatible and conductive electrochemical platform, a single-stranded DNA (ss-DNA)/graphene nanocomposite was fabricated to realize the direct electrochemistry of immobilized horseradish peroxidase (HRP; see schematic representation; GC: glassy carbon).

Host–Guest Systems



Crowning glory: Complexes of mono- and diorganotin dications were prepared by using [16]crown-5 as a protecting group. The molecular structures of the complexes show that the tin(IV) atom is trapped within the cavity of the crown ether ring. Notably, two of the compounds prepared are the first compounds that contain a monomeric monoorganotin(IV) dication and a monomeric monoorganotin hydroxide (one of which is depicted, with the omission of perchlorate anions).

Sensors

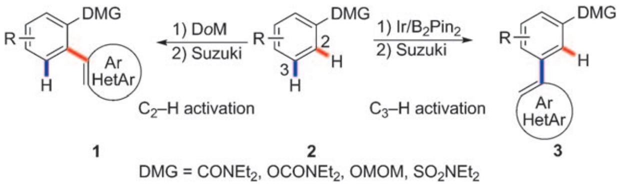


Reusable sensor: A reusable DNA single-walled carbon nanotube (SWNT)-based fluorescent sensor for Ag^+ and cysteine (Cys) has been designed by the combination of C–Ag^+–C (C = cytosine) coordination chemistry and Cys–Ag^+ complex formation (see figure).

Homogeneous Catalysis

*T. E. Hurst, T. K. Macklin, M. Becker, E. Hartmann, W. Kügel, J.-C. Parisienne-La Salle, A. S. Batsanov, T. B. Marder, V. Snieckus** .... 8155 – 8161

Iridium-Catalyzed C–H Activation versus Directed *ortho* Metalation: Complementary Borylation of Aromatics and Heteroaromatics

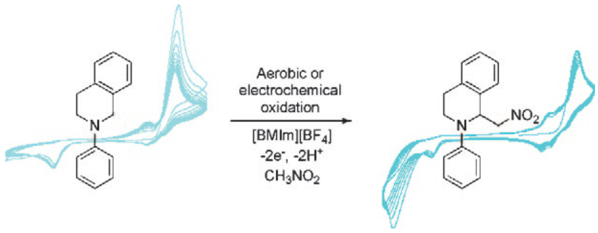


D*o*M versus C–H activation: Systematic studies are presented demonstrating the complementarity of directed *ortho* metalation (D*o*M) and Ir-catalyzed strategies for the provision of borylated aromatics and their subsequent Suzuki–Miyaura coupling reactions. A new concept that overcomes the otherwise problematic production of isomeric borylated product mixtures is presented.

Ionic Liquids

O. Baslé, N. Borduas, P. Dubois, J. M. Chapuzet, T.-H. Chan, J. Lessard, C.-J. Li** .... 8162 – 8166

Aerobic and Electrochemical Oxidative Cross-Dehydrogenative-Coupling (CDC) Reaction in an Imidazolium-Based Ionic Liquid

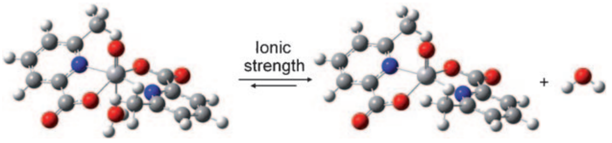


Ionic efficiency: The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm][BF$_4$] has demonstrated high efficiency when applied as a solvent for oxidative nitro-Mannich carbon–carbon bond formation (see scheme). The copper-catalyzed cross-dehydrogenative coupling (CDC) and the potentiostatic electrolysis in the ionic liquid afforded the desired product with a high yield.

Vanadium Chemistry

*S. Gorelsky, G. Micera, E. Garribba** .... 8167 – 8180

The Equilibrium Between the Octahedral and Square Pyramidal Form and the Influence of an Axial Ligand on the Molecular Properties of V^{IV}O Complexes: A Spectroscopic and DFT Study

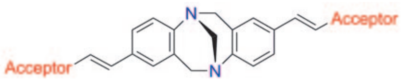


***trans* Octahedral or square pyramidal?** The previously unreported equilibrium between the *trans* octahedral and square-pyramidal forms of bis-chelated V^{IV}O complexes is described (see figure). Such an equilibrium depends on the ionic strength of the solution. Whereas the square-pyramidal species is characterised by "normal" EPR parameters, the octahedral form shows an anomalously low value of the ^{51}V anisotropic hyperfine coupling constant (A_z). DFT methods confirm that, in contrast to what was previously believed, the presence of an axial ligand can lower the A_z value.

Chromophores

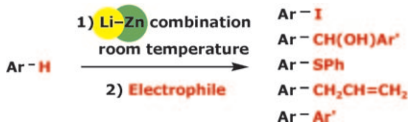
S. Sergeyev, D. Didier, V. Boitsov, A. Teshome, I. Asselberghs, K. Clays, C. M. L. Vande Velde, A. Plaquet, B. Champagne* .... 8181 – 8190

Symmetrical and Nonsymmetrical Chromophores with Tröger's Base Skeleton: Chiroptical, Linear, and Quadratic Nonlinear Optical Properties—A Joint Theoretical and Experimental Study



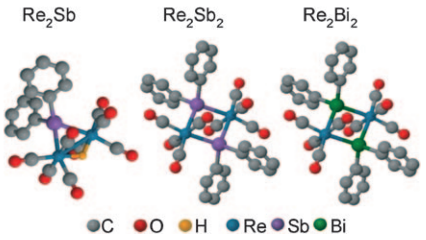
V-shaped chromophores: Chiral, V-shaped push–pull chromophores derived from 6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (Tröger's base skeleton) are prepared in both racemic and enantiomerically pure form (see graphic). Their second-order nonlinear optical properties were investigated with the aid of hyper-Rayleigh scattering.

A perfect combo: The ability of various mixtures of lithium and zinc compounds to deproto-metalate aromatics, including heterocycles, was studied (see image). The reactivity of such generated metalated species depends on different parameters, such as the nature of the aromatic itself, the electrophile used, as well as the basic mixture employed.



Metalation

Single sites: The interaction between the organometallic cluster complexes (see figure) and the silica support is the driving force that leads to the generation of Re^0 single sites, which are active for the ammoxidation of 3-picoline to nicotinonitrile (which is a precursor for vitamin B$_3$). The key step in the decomposition of the dirhenium precursor complexes is the loss of the phenyl groups from the oxophile and its subsequent binding to the silica surface.



Single-Site Catalysts

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