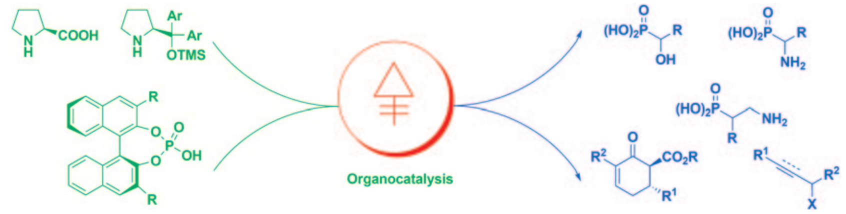
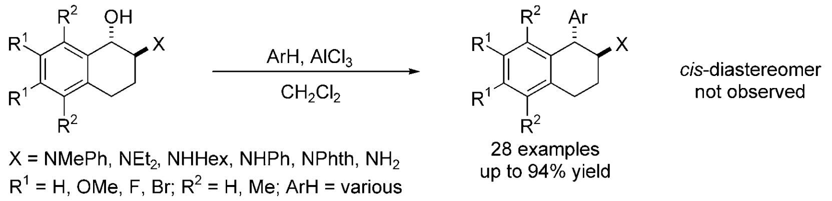
REVIEWS

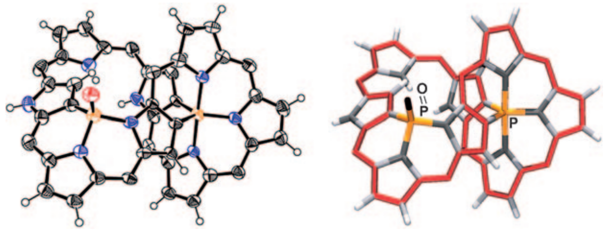


From the philosopher's stone to phosphorus: Organophosphorus compounds have found applications in asymmetric organocatalysis for the synthesis of optically active compounds of synthetic or biological importance. The aim of this review article is to present recent contributions to this developing field of chemistry and to point out synthetic advantages of methodologies developed so far.

COMMUNICATIONS



Friedel–Crafts protocols for the intermolecular, *trans*-selective benzylic arylation of tetralin systems are described (see scheme). The protocols have broad substrate scope and the use of enantiopure substrates allows the preparation of *trans*-aryl-substituted tetralins in high *ee*.

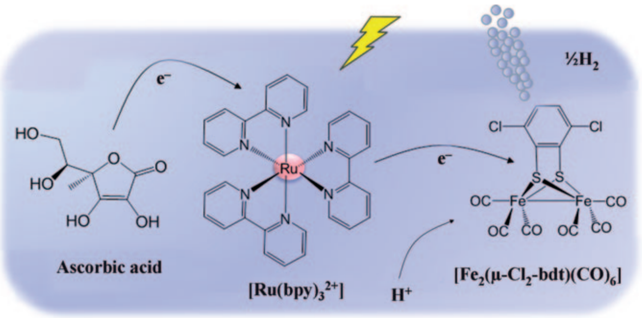


Bisphosphorus complexes: Phosphorus complexes of octaphyrin were prepared upon the treatment of [36]octaphyrin(1.1.1.1.1.1.1.1) with PCl$_3$ in the presence of amine and a small amount of water (see figure). Reversible redox interconversions between 38π- and 40π-electronic states were demonstrated.

Hydrogen Production

D. Streich, Y. Astuti, M. Orlandi, L. Schwartz, R. Lomoth, L. Hammarström, S. Ott** 60–63

High-Turnover Photochemical Hydrogen Production Catalyzed by a Model Complex of the [FeFe]-Hydrogenase Active Site

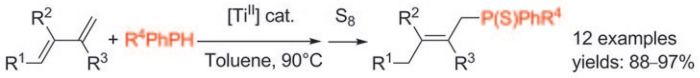


Lifting the diiron curtain: 200 equivalents of H_2 per catalyst at a maximum turnover rate of 3.7 H_2 per minute can be obtained in a light-driven proton reduction process in near-neutral H_2O/DMF (pH 5.5) by using an [FeFe]-hydrogenase active-site model complex as the catalyst (see scheme).

Homogeneous Catalysis

*A. Perrier, V. Comte, C. Moïse, P. Le Gendre** 64–67

First Titanium-Catalyzed 1,4-Hydrophosphination of 1,3-Dienes

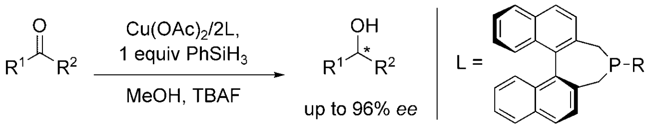


Titanium complexes outshine other catalysts: Titanium complexes have been found to catalyze 1,4-hydrophosphination of dienes, which is thought to proceed through an allyl intermediate (see scheme). Unprecedented regioselectivities (1,4- vs. 1,2-) are reached by using $[TiCp_2(PMe_3)_2]$ or a titanocene complex bearing a pendant phosphine tether as catalysts.

Homogeneous Catalysis

*K. Junge, B. Wendt, D. Addis, S. Zhou, S. Das, M. Beller** 68–73

Copper-Catalyzed Enantioselective Hydrosilylation of Ketones by Using Monodentate Binaphthophosphepine Ligands

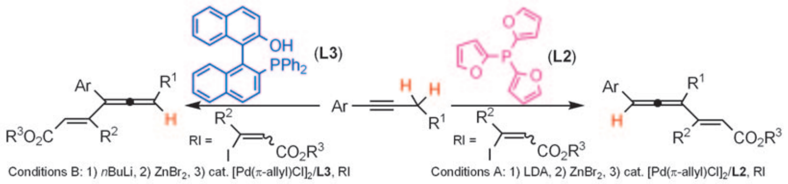


No base required: The first copper-catalyzed asymmetric hydrosilylation of carbonyl compounds by using monodentate binaphthophosphepine ligands is presented. After optimization of the reaction parameters, high yields and enantioselectivities (up to 96 % *ee*) for a broad range of aryl alkyl, cyclic, heterocyclic, and aliphatic ketones are achieved without a base.

Cross-Coupling

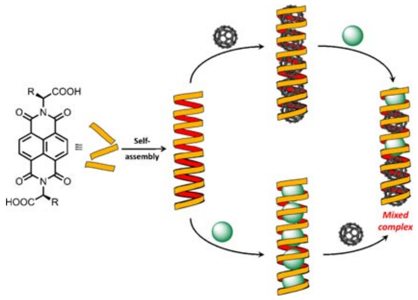
*J. Zhao, Y. Yu, S. Ma** 74–80

Ligand Effects on the Pd-Catalyzed Cross-Coupling Reaction of 3-Iodoalk-2-enoates with Propargyl/1,2-Allenylic Metallic Species: An Efficient Regiodivergent Synthesis of 2,4,5-Trienoates

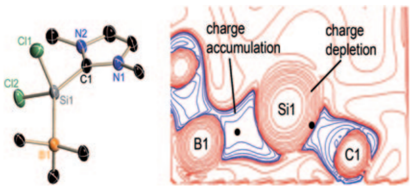


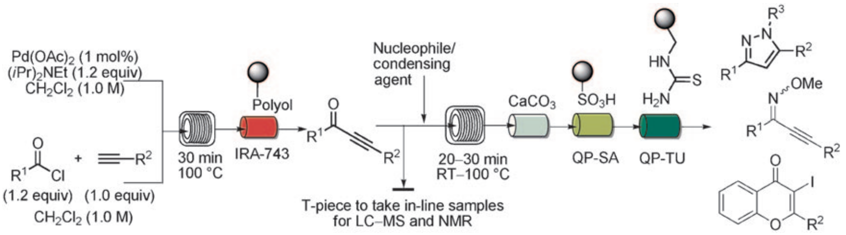
A ligand makes a big difference: The 1,3-lithium shift of propargyl/1,2-allenyl lithium has been tuned and applied in a subsequent transmetalation and Pd-catalyzed Negishi coupling reaction with 3-iodoalk-2-enoates to give a highly regioselective and regiodivergent synthesis of 2,4,5-trienoates. It was discovered that ligands play a very important role in the cross-coupling reactions with respect to both regioselectivity and reactivity.

Unlikely bedfellows: Naphthalenediimide-based supramolecular nanotubes act as size-selective receptors for ion pairs, as demonstrated by competition experiments with C_{60} (see picture). Fullerene forms mixed complexes inside the cavity of the nanotubes in the presence of the anion and ammonium ions of the appropriate size.



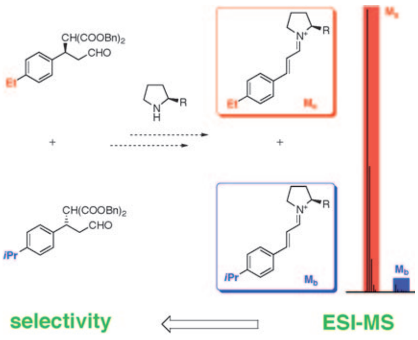
$SiCl_2$ as a simultaneous σ-donor and -acceptor: The reaction of the Lewis base stabilized dichlorosilylene L→$SiCl_2$ with $B(C_6F_5)_3$ (L = imidazol-2-ylidene derivative) afforded the first silylene donor acceptor L→$SiCl_2$→$B(C_6F_5)_3$ complex (shown here). Charge density analysis revealed that the two C→Si and Si→B donor bonds are of considerably different quality. However, plain bond length consideration might suggest simple C–Si and Si–B single bonds.

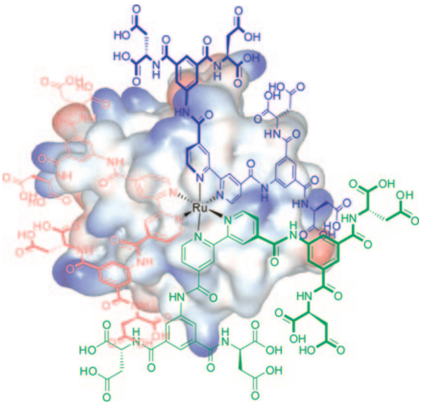




Multi-step in flow: The palladium-catalysed acylation of terminal alkynes for the synthesis of yne–ones as well as their further transformation to various heterocycles in a continuous-flow mode is presented. Furthermore, an extension of the simple flow configuration that allows for easy batch splitting and the generation of a heterocyclic library is described (see scheme).

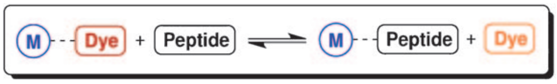
Shortcut to chiral catalysts: An efficient combinatorial strategy based on back reaction screening by ESI-MS allows rapid evaluation of organocatalysts for the asymmetric Michael addition to α,β-unsaturated aldehydes (see scheme). An unexpected nonlinear effect has been observed in this reaction, resulting from a double nucleophilic–electrophilic activation mechanism involving two catalyst molecules.



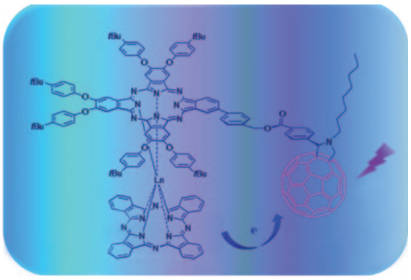


Protein surface recognition: Functionalised Ru^{II} tris-(bipyridine) complexes are shown to act as high-affinity (2 nM) and selective receptors for the surface of cytochrome c (see figure) as compared to a panel of other proteins.

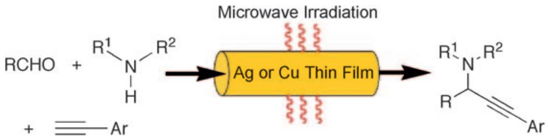
FULL PAPERS



Fingerprints of peptides: Sensor arrays composed of transition-metal complexes and fluorescent dyes allow the detection of peptides in aqueous solutions (see scheme) or in deproteinized human serum.



Charge transfer from the sandwich: A stepwise procedure has been used to prepare a series of heteroleptic double-decker lanthanide(III) bis-(phthalocyaninato)–C_{60} dyads, which show photoinduced charge transfer after excitation of the fullerene unit.

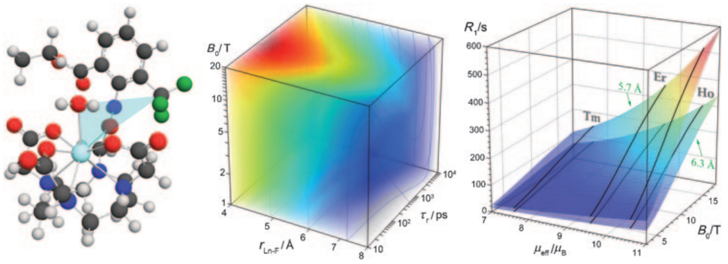


Microwave chemistry: A general, efficient protocol has been developed for the preparation of propargyl amines by using either gold or copper thin films as the catalyst. The process is promoted by microwave-assisted continuous-flow organic synthesis (see scheme).

Magnetic Resonance Imaging

K. H. Chalmers, E. D. Luca, N. H. M. Hogg, A. M. Kenwright, I. Kuprov, D. Parker,* M. Botta, J. I. Wilson, A. M. Blamire* . . . 134 – 148

Design Principles and Theory of Paramagnetic Fluorine-Labelled Lanthanide Complexes as Probes for ^{19}F Magnetic Resonance: A Proof-of-Concept Study



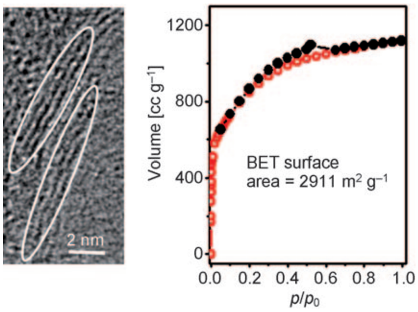
Shift and relax: A series of CF_3-labelled paramagnetic lanthanide(III) complexes, in which enhanced sensitivity is gained by increasing the relaxation rate of the ^{19}F nucleus, has been defined. Careful positioning of the fluorine leads to enhanced chemical shift non-equivalence in responsive systems suitable for shift imaging.

Materials Science

*K. Raidongia, A. Nag, K. P. S. S. Hembram, U. V. Waghmare, R. Datta, C. N. R. Rao** .... 149 – 157

BCN: A Graphene Analogue with Remarkable Adsorptive Properties

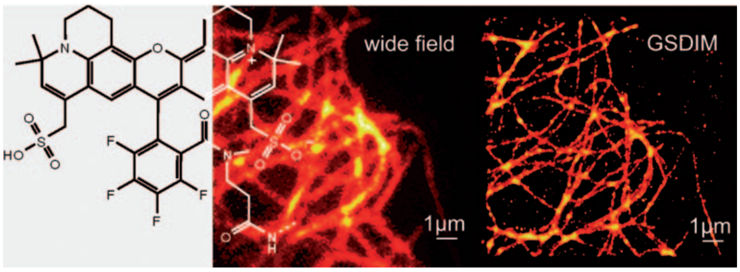
Stripped apart: Few-layer BCN has been prepared by simple chemical means. Experimental and theoretical studies establish BCN as a graphene analogue with interesting electronic and magnetic properties. Few-layer BCN exhibits very high surface area and a high propensity for CO_2 adsorption (○: adsorption, ●: desorption; see figure).



Fluorescent Probes

K. Kolmakov, V. N. Belov, J. Bierwagen, C. Ringemann, V. Müller, C. Eggeling, S. W. Hell** .... 158 – 166

Red-Emitting Rhodamine Dyes for Fluorescence Microscopy and Nanoscopy

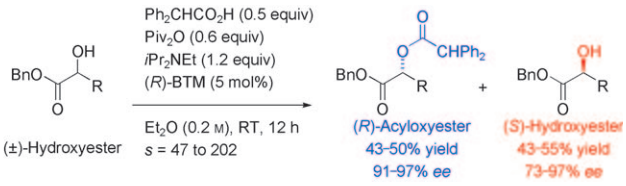


Optical nanoscopy labels: New rhodamine dyes and their reactive derivatives are proposed as efficient photostable fluorescent labels for imaging in the red optical region, which is very important for biological studies (see picture). The dyes feature high fluorescence quantum yields and photostability in solution and attached to antibodies, and perform well in far-field nanoscopic techniques, such as GSDIM and fluorescence correlation spectroscopy.

Kinetic Resolution

I. Shiina, K. Nakata, K. Ono, M. Sugimoto, A. Sekiguchi* . . . 167 – 172

Kinetic Resolution of the Racemic 2-Hydroxyalkanoates Using the Enantioselective Mixed-Anhydride Method with Pivalic Anhydride and a Chiral Acyl-Transfer Catalyst

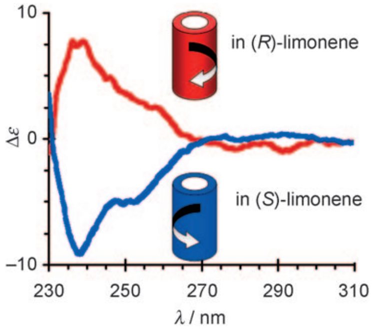


There is no need for a *sec*-phenethyl alcohol moiety to achieve high *ee* values in a kinetic resolution. The combined use of diphenylacetic acid, pivalic anhydride, and (+)-(*R*)-benzotetramisole effectively produce (*R*)-2-acyloxyesters and (*S*)-2-hydroxyesters (*s*-values = 47–202). This protocol directly provides the desired chiral 2-acyloxyesters from racemic 2-hydroxyesters with achiral diarylacetic acid by generating the mixed anhydrides.

Chiral Nanotubes

*B. Isare, M. Linares, L. Zargarian, S. Fermandjian, M. Miura, S. Motohashi, N. Vanthuyne, R. Lazzaroni, L. Bouteiller** . . 173 – 177

VIP **Chirality in Dynamic Supramolecular Nanotubes Induced by a Chiral Solvent**

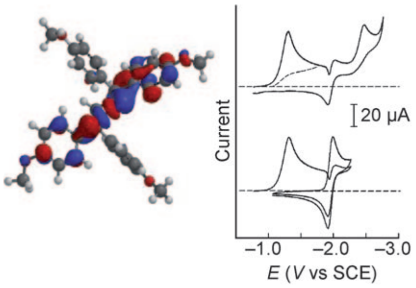


Majority-rules effect: We report a strong majority-rules effect in the formation of chiral dynamic nanotubes from chiral bisurea monomers. The same helical nanotubes can be obtained from racemic monomers in a chiral solvent (see figure). Competition experiments revealed the relative strength of the helical bias induced by the chiral monomer or by the chiral solvent.

Radical Ions

*D. L. B. Stringle, D. C. Magri, M. S. Workentin** . . . . 178 – 188

VIP **Efficient Homogeneous Radical-Anion Chain Reactions Initiated by Dissociative Electron Transfer to 3,3,6,6-Tetraaryl-1,2-dioxanes**

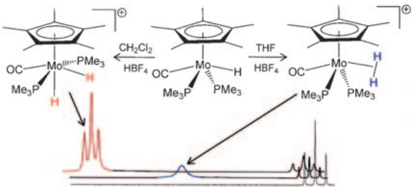


Electron transfer to endoperoxides: Electron transfer (ET) reduction of the O–O in a series of tetraaryl endoperoxides generates distonic radical-anion intermediates by cyclic voltammetry (see figure). A rapid β-scission fragmentation competes with ET from the electrode yielding an alkene, a substituted benzophenone, and a benzophenone radical anion, which initiates a propagating homogenous radical-anion chain reaction.

Non-Covalent Interactions

P. A. Dub, N. V. Belkova, O. A. Filippov, J.-C. Daran, L. M. Epstein, A. Lledós, E. S. Shubina, R. Poli** . . . . 189 – 201

Solvent-Dependent Dihydrogen/Dihydride Stability for $[Mo(CO)(Cp^*)H_2(PMe_3)_2]^+[BF_4]^-$ Determined by Multiple Solvent···Anion···Cation Non-Covalent Interactions

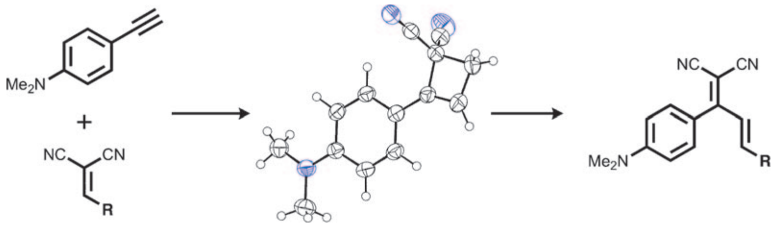


The relative stability of classical and non-classical isomers of $[Mo(CO)(Cp^*)H_2(PMe_3)_2]^+[BF_4]^-$ is fine-tuned by subtle solvent differences through a network of non-covalent solvent···$[BF_4]^-$···$[Mo(CO)(Cp^*)H_2(PMe_3)_2]^+$ interactions, in which the solvent and the cation compete as proton donors for the same electron density in BF_4^-.

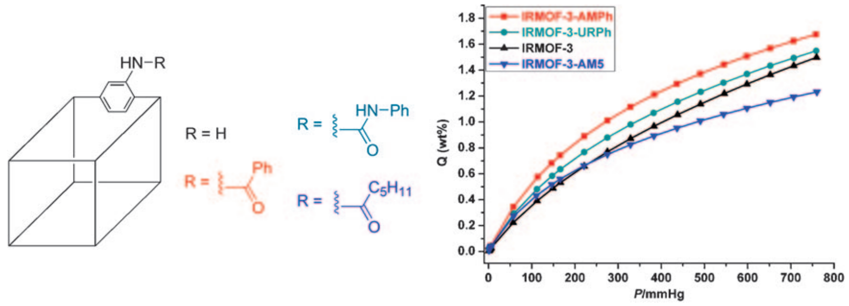
Reaction Mechanisms

*Y.-L. Wu, P. D. Jarowski, W. B. Schweizer, F. Diederich** . . . . 202 – 211

Mechanistic Investigation of the Dipolar [2+2] Cycloaddition–Cycloreversion Reaction between 4-(*N*,*N*-Dimethylamino)phenylacetylene and Arylated 1,1-Dicyanovinyl Derivatives To Form Intramolecular Charge-Transfer Chromophores



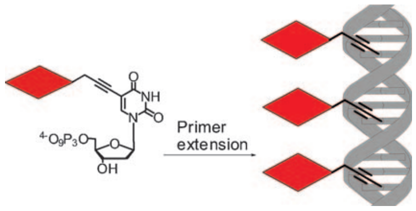
Intermediate trapped! A detailed investigation of the cycloaddition–cycloreversion reaction between *N*,*N*-dimethylanilinoacetylene and arylated 1,1-dicyanovinyl derivatives elucidated its bimolecular, dipolar reaction mechanism, in which the relative height of reaction barriers is highly sensitive to the substituents. In one case, the cyclobutene formed in the cycloaddition step could be isolated as a crystalline solid and its structure analyzed (see scheme).



Interior design: Metal–organic frameworks (MOFs) that are subjected to postsynthetic modification are shown to have different hydrogen adsorption properties (see picture). These differences are related to both the degree of modification and the topology of the MOF. These studies provided the basis for the development of a structure–activity relationship for designing the interiors of MOFs for maximum hydrogen storage.

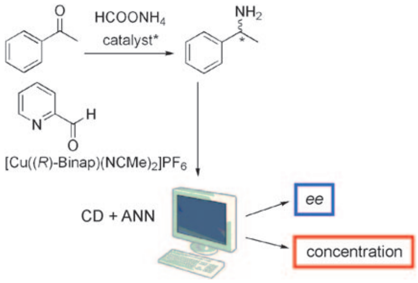
Metal–Organic Frameworks

DNA hybrid materials: DNA polymerases accept nucleotides carrying polymer moieties linked to the nucleobase to generate new DNA-based materials of high molecular weight, modification density and defined structure (see figure; red diamond = polymer moiety).



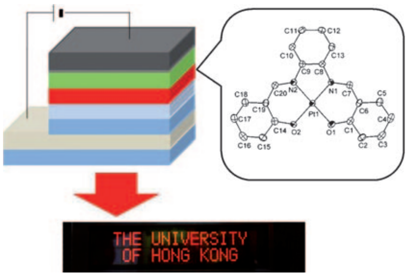
DNA Copolymers

New protocols: By employing pattern-recognition techniques based on the monitorization of MLCT bands of simple receptors in the circular dichroism (CD) spectra, rapid and simultaneous *ee* and concentration determination of chiral amines was accomplished (see scheme). This protocol was also applied to determine the *ee* of the crude products of an asymmetric catalytic reaction by simple derivatization.



Chirality

Glow in the dark: Phosphorescent platinum(II) Schiff base complexes have been prepared and their photophysical properties investigated. They are thermally stable, with decomposition temperatures up to 495 °C, and exhibit high emission quantum yields (up to 0.27) in solution. Their applications in OLEDs were investigated (see figure).

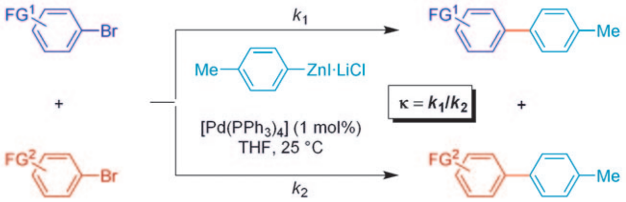


High Efficiency OLEDs

Reaction Mechanisms

*Z.-B. Dong, G. Manolikakes, L. Shi, P. Knochel, H. Mayr** .... 248 – 253

Structure–Reactivity Relationships in Negishi Cross-Coupling Reactions

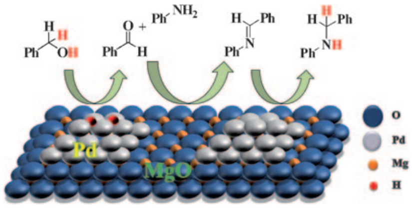


Competition experiments with 18 substituted bromobenzenes show that 4-CN accelerates the oxidative addition by a factor of 326, whereas 4-OCH_3 retards it by a factor of 3.8 (see picture).

Heterogeneous Catalysis

A. Corma, T. Ródenas, M. J. Sabater** .... 254 – 260

A Bifunctional Pd/MgO Solid Catalyst for the One-Pot Selective N-Monoalkylation of Amines with Alcohols

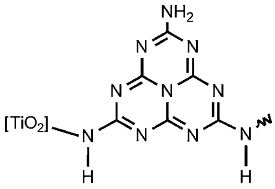


A capable catalyst: A Pd/MgO catalyst can perform the N-monoalkylation of amines with high selectivity and turnover frequencies—about four times higher than homogeneous Ru or Ir catalysts under similar reaction conditions (see image).

Photocatalysis

*D. Mitoraj, H. Kisch** .... 261 – 269

On the Mechanism of Urea-Induced Titania Modification

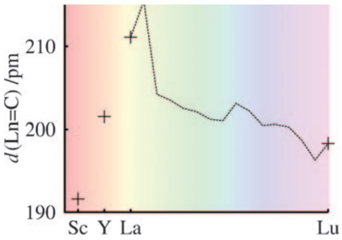


Concentration is crucial: Contrary to previous reports, visible-light photocatalytic activity of “N-doped” titania prepared from urea does not originate from the presence of nitridic, amidic, and nitrogen oxide species or lattice defects, but from condensed aromatic *s*-triazine compounds (see scheme). The mechanistic role of the polytriazine component depends on its-concentration.

Bonding

B. O. Roos, P. Pyykkö** ...... 270 – 275

Bonding Trends in Molecular Compounds of Lanthanides: The Double-Bonded Carbene Cations $LnCH_2^+$ (Ln = Sc, Y, La–Lu)

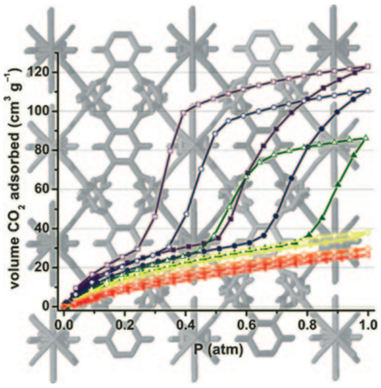


Setting a trend! CASPT2 calculations on carbene cations of lanthanides (Sc, Y, La–Lu) revealed well-developed double bonds (see figure), mainly built on the 5d orbitals of La–Lu. The 4f shell acts as a spin counterweight and an electron reservoir.

Metal-Organic Frameworks

*K. L. Mulfort, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp** .... 276 – 281

An Interpenetrated Framework Material with Hysteretic CO_2 Uptake

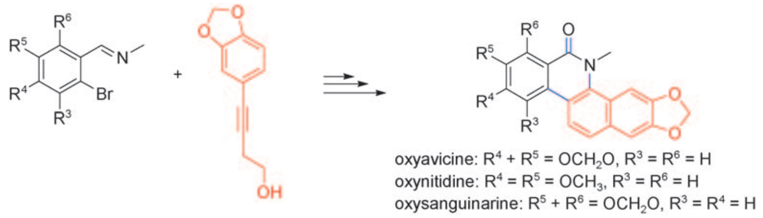


MOFs on the move: A new, twofold interpenetrated metal–organic framework (MOF) material has been synthesized that demonstrates dramatic steps in the adsorption and hysteresis in the desorption of CO_2. Powder X-ray diffraction measurements and pair distribution function analysis indicate that structural changes upon CO_2 sorption most likely involve the interpenetrated frameworks moving with respect to each other.

Total Synthesis

*R. P. Korivi, C.-H. Cheng** 282–287

Protecting-Group-Free Total Synthesis of Isoquinoline Alkaloids by Nickel-Catalyzed Annulation of *o*-Halobenzaldimine with an Alkyne as the Key Step

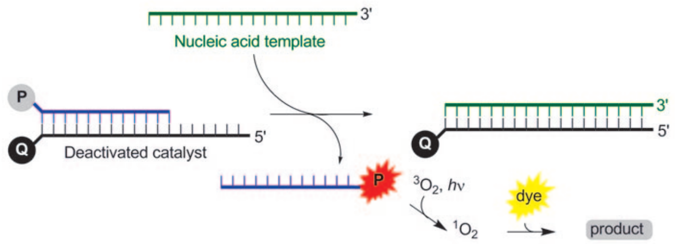


An efficient four-step total synthesis procedure for isoquinolinone alkaloids was developed (see scheme), which features a regioselective nickel-catalyzed formation of the isoquinolinium salt from the corresponding *o*-bromobenzaldimine and alkyne, in situ conversion to isoquinolinone, oxidation of the primary alcohol functional group followed by an acid-catalyzed intramolecular ring-closing reaction.

Photosensitizers

*D. Arian, E. Cló, K. V. Gothelf, A. Mokhir** 288–295

A Nucleic Acid Dependent Chemical Photocatalysis in Live Human Cells

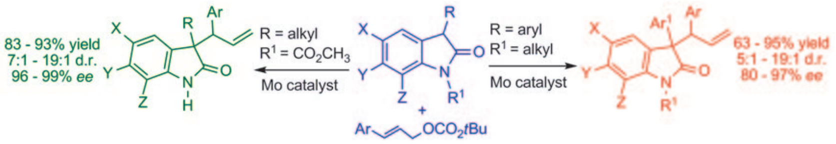


Alive and light sensitive: A nucleic acid dependent photosensitizer was developed that is able to generate over 6000 equivalents of toxic singlet oxygen per equivalent of catalyst and is highly sequence specific (see figure; P: photosensitizer; Q: quencher). The activity of this compound in live human cells is efficiently controlled by specific endogeneous ribonucleic acids. This is the first example of a live-cell-compatible gene-specific photosensitizer.

Stereoinduction

B. M. Trost, Y. Zhang* 296–303

Catalytic Double Stereoinduction in Asymmetric Allylic Alkylation of Oxindoles

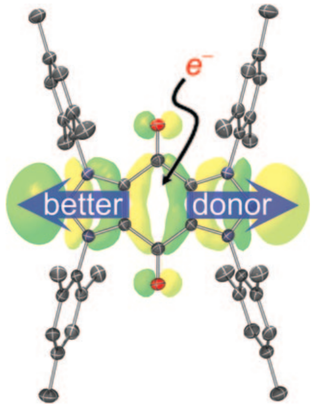


Crank up the stereo system: A highly regio-, diastereo-, and enantioselective allylic alkylation reaction of 3-monosubstituted oxindoles catalyzed by molybdenum is described (see scheme). The reaction is affected by electronic and steric variations of the nucleophile. Products from this reaction, containing vicinal quaternary-tertiary stereogenic centers, are valuable synthetic intermediates and should find utility in alkaloid synthesis.

N-Heterocyclic Carbenes

A. G. Tennyson, R. J. Ono, T. W. Hudnall, D. M. Khramov, J. A. V. Er, J. W. Kamplain, V. M. Lynch, J. L. Sessler, C. W. Bielawski** .... 304 – 315

Quinobis(imidazolylidene): Synthesis and Study of an Electron-Configurable Bis(N-Heterocyclic Carbene) and Its Bimetallic Complexes

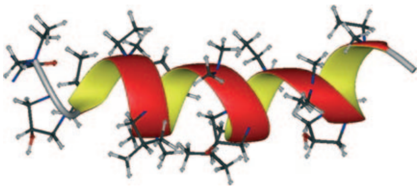


Pump it up! 1,1′,3,3′-Tetramesitylquinobis(imidazolylidene) (**1**), an electron-configurable, ditopic N-heterocyclic carbene (NHC), was obtained in two steps. Bimetallic complexes of **1** with FcN_3 (Fc = ferrocenyl), FcNCS, [M(cod)Cl] (M = Rh, Ir; cod = 1,5-cyclooctadiene), and $[M(CO)_2Cl]$ (M = Rh, Ir) units were then prepared. Their spectral and structural data are similar to those of bis(NHC)-supported analogues, yet reduction of the quinone gave increased electron density on the metal atom (see picture).

Peptide Synthesis

*M. De Zotti, F. Damato, F. Formaggio, M. Crisma, E. Schievano, S. Mammi, B. Kaptein, Q. B. Broxterman, P. J. Felock, D. J. Hazuda, S. B. Singh, J. Kirschbaum, H. Brückner, C. Toniolo** .... 316 – 327

Total Synthesis, Characterization, and Conformational Analysis of the Naturally Occurring Hexadecapeptide Integramide A and a Diastereomer

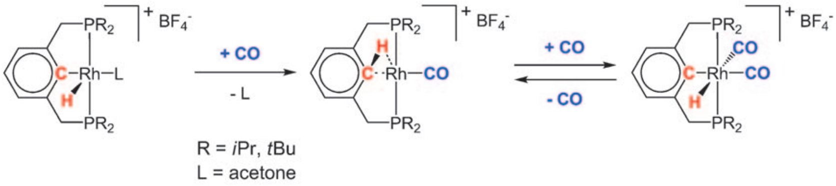


A peptide inhibitor of HIV-1 integrase: Total synthesis, extensive characterization, and detailed conformational analysis (by using circular dichroism, FTIR absorption, 2D NMR spectroscopy, and X-ray diffraction techniques) of the hexadecapeptide integramide A (see graphic) and selected segments thereof have been carried out. Valuable information aimed at a deeper understanding of the mode of interaction of integramide A with its target enzyme is presented.

C−H Activation

M. Montag, I. Efremenko, R. Cohen, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, Y. Ben-David, H. Salem, J. M. L. Martin, D. Milstein** .... 328 – 353

Effect of CO on the Oxidative Addition of Arene C−H Bonds by Cationic Rhodium Complexes

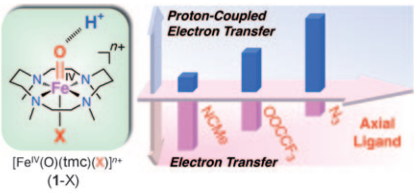


CO(unterintuitive) effect: CO is commonly viewed as a strong π-acceptor ligand that lowers the electron density on a transition-metal atom, thereby inhibiting oxidative addition and promoting reductive elimination. New experimental and computational evidence involving cationic rhodium pincer complexes (see scheme) paints a surprisingly different picture.

Bioinorganic Chemistry

S. Fukuzumi, H. Kotani, T. Suenobu, S. Hong, Y.-M. Lee, W. Nam** .... 354 – 361

Contrasting Effects of Axial Ligands on Electron-Transfer Versus Proton-Coupled Electron-Transfer Reactions of Nonheme Oxoiron(IV) Complexes

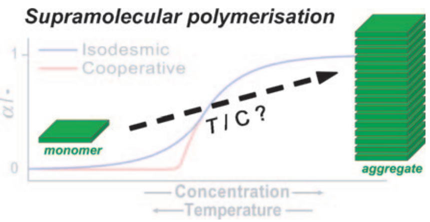


tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane

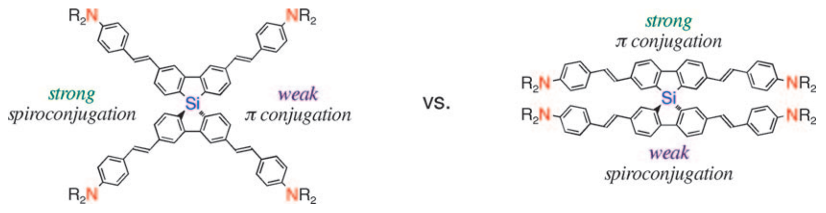
Counterintuitive reactivities: The rates of electron transfer (ET) and proton-coupled electron-transfer (PCET) in the reactions of with ferrocene derivatives are markedly affected by the electron-donating ability of the axial ligands (X) in opposite directions (see figure); the electron-donating axial ligand decelerates the ET rate in the reactions, but enhances the PCET reactivity of **1**-X in the presence of acid.

Self-Assembly

Self-assembly mechanisms of a self-assembled system were studied by concentration- and temperature-dependent measurements. Both methods were evaluated to determine their effectiveness in identifying and quantifying the self-assembly mechanism for isodesmic and cooperative systems (see figure). For a fast and unambiguous determination of the assembly mechanism and its thermodynamic parameters, temperature-dependent measurements are more appropriate.



Silafluorenes



Spiro- versus π conjugation: Silafluorenes and spirobisilafluorenes (see picture) bearing aminostyryl groups at the 2,7- or 3,6-positions were synthesized. Their UV/Vis data reveal the influence of σ(Si–C)*–π* hyperconjugation and spiroconjugation on their photophysical properties. Their fluorescence properties are compatible with UV/Vis absorption data, except for the 3,6-substituted spirobisilafluorene, for which DFT calculations on a model compound revealed the presence of spiroconjugation.

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* Author to whom correspondence should be addressed

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