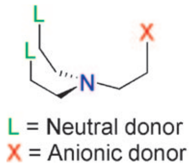
MINIREVIEW

Coordination Chemistry

*W. A. Chomitz, J. Arnold** 2020–2030

Use of Tetradentate Monoanionic Ligands for Stabilizing Reactive Metal Complexes



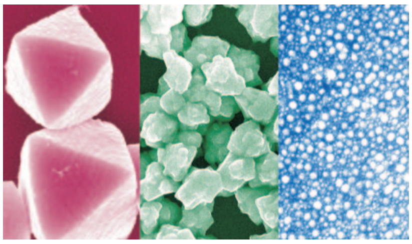
Ligand scaffolding: The chemist's ability to choose from a wide range of supporting ligands is an important factor in designing new metal complexes. The introduction of new ligand scaffolds with different donor types and coordination numbers allows for the expansion of reaction chemistry at metal centers. This article surveys the use of the tetradentate monoanionic (TMDA) ligands (shown here) with main-group, transition-metal, and f-block elements.

COMMUNICATIONS

Nanoparticles

*B. Kowalczyk, A. M. Kalsin, R. Orlik, K. J. M. Bishop, A. Z. Patashinskii, A. Mitus, B. A. Grzybowski** 2032–2035

Size Selection During Crystallization of Oppositely Charged Nanoparticles

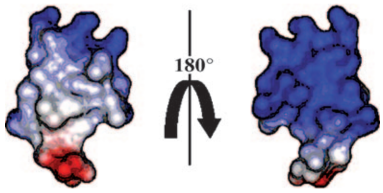


Opposites attract (selectively): Oppositely charged nanoparticles characterized by different size distributions form 3D supracrystals (see figure) only if the distributions overlap. Crystal quality decreases rapidly with decreasing degree of overlap, and, irrespective of the ratio of particle diameters/charges, no crystals are observed for non-overlapping distributions.

Peptide Antibiotics

A. Bhunia, A. Ramamoorthy, S. Bhattacharjya** 2036–2040

Helical Hairpin Structure of a Potent Antimicrobial Peptide MSI-594 in Lipopolysaccharide Micelles by NMR Spectroscopy

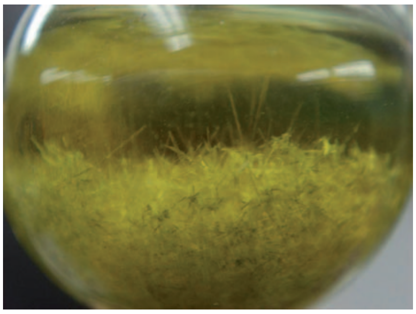


Essential understanding: Elucidation of structural requirements and interactions of antimicrobial peptides with lipopolysaccharide (LPS) are essential to understand the mechanism of action of antimicrobial peptides. The highly active antimicrobial peptide MSI-594 (see figure for electrostatic potential surface) acquires a novel helical hairpin structure in complex with LPS. The structure and interactions of MSI-594 with LPS presented here provide important insights into the mechanism of outer membrane permeabilization by antimicrobial peptides.

C−C Coupling

*X.-Y. Chen, C. Barnes, J. R. Dias, T. C. Sandreczki** 2041–2044

Investigation of sp^2–sp Coupling for Electron-Enriched Aryl Dihalides under Oxygen-Free Sonogashira Coupling Reaction Conditions Using a Two-Chamber Reaction System

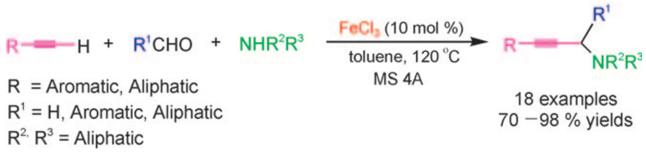


Triethylamine hydroiodide crystals were formed during Sonogashira reactions; after complete reaction the solution retains a characteristic light color (see picture). Very sluggish Sonogashira reactions of electron-enriched aryl diiodides have been carried out in high yield in an oxygen-free, two-chamber reaction system. The formation of triethylamine hydroiodide crystals was monitored to determine the completion of reaction.

Coupling Reactions

*P. Li, Y. Zhang, L. Wang** 2045 – 2049

Iron-Catalyzed Ligand-Free Three-Component Coupling Reactions of Aldehydes, Terminal Alkynes, and Amines

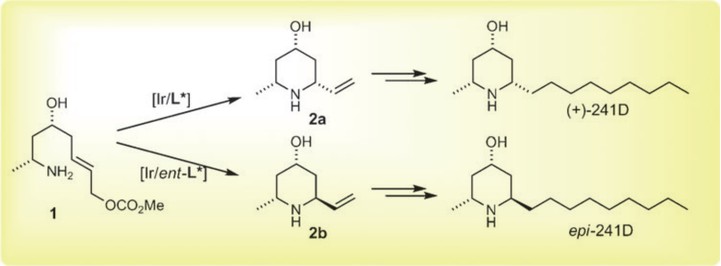


A tri-umph in many respects: The iron-catalyzed ligand-free, one-pot three-component coupling reactions of aldehydes, terminal alkynes, and amines in the presence of 4 A molecular sieves yields the corresponding propargylamines in good to excellent yields, displays a broad substrate scope, and is economical and environmentally friendly (see scheme).

Asymmetric Catalysis

*C. Gnamm, C. M. Krauter, K. Brödner, G. Helmchen** .... 2050 – 2054

Stereoselective Synthesis of 2,6-Disubstituted Piperidines Using the Iridium-Catalyzed Allylic Cyclization as Configurational Switch: Asymmetric Total Synthesis of (+)-241 D and Related Piperidine Alkaloids

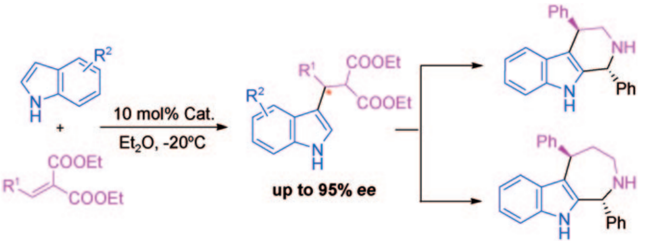


Pressing the configurational switch: Use of enantiomeric Ir catalysts allows the vinylpiperidine building blocks **2a** and **2b** to be synthesized with high selectivity. Total syntheses of the dendrobate alkaloid (+)-241 D, its C6-epimer, and a spruce alkaloid are presented as applications.

Asymmetric Synthesis

*Y. Liu, D. Shang, X. Zhou, X. Liu, X. Feng** .... 2055 – 2058

Enantioselective Friedel–Crafts Alkylation of Indoles with Alkylidene Malonates Catalyzed by *N,N'*-Dioxide–Scandium(III) Complexes: Asymmetric Synthesis of *β*-Carbolines



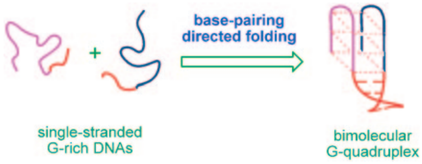
An efficient catalytic asymmetric Friedel–Crafts alkylation of indoles with alkylidene malonates has been developed by using a chiral *N,N'*-dioxide–Sc(OTf)$_3$ complex as the catalyst (see scheme). Some optically active intermediates containing the indole skeleton have been synthesized, such as indolepropionic acid, tryptamines, and *β*-carbolines. The coordination between the scandium atom and the chiral *N,N'*-dioxide compound has been revealed by X-ray structure analysis.

DNAzymes

*T. Li, E. Wang, S. Dong** ... 2059 – 2063

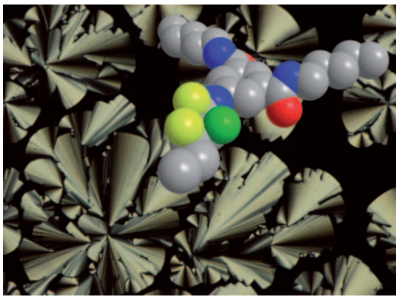
Base-Pairing Directed Folding of a Bimolecular G-Quadruplex: New Insights into G-Quadruplex-Based DNAzymes

Base pairs, magic hands: An additional base-pairing duplex is utilized to control the folding topologies of a bimolecular G-quadruplex formed by two G-rich single-stranded DNAs (see picture), which is dependent on the position of base pairs. This study clearly reveals an important intrinsic role of additional base pairs in the G-quadruplex structure, and also provides a clue to the formation mechanism of the G-quadruplex-based DNAzyme.

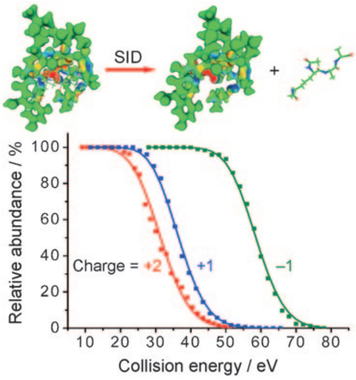


FULL PAPERS

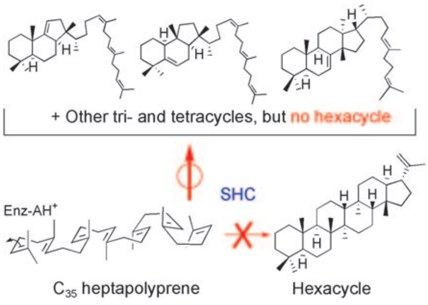
Just five steps! The synthesis of a phosphonate-linked aminoglycoside-coenzyme A derivative (see scheme) that includes a Michael addition in water has been realized in just five steps.



Molecular organization: Chiral benzene tricarboxamides with methyl substituents at defined positions self-assemble into supramolecular polymers of preferred helicity by three-fold α-helical-type hydrogen bonding. The odd–even effect is operative and all derivatives are liquid crystalline showing a Col$_{ho}$ phase (see figure).



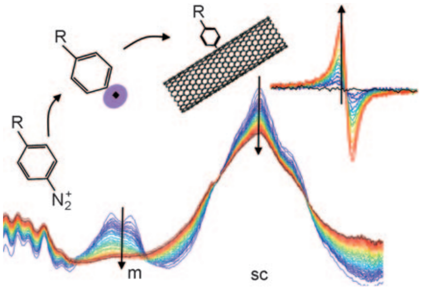
Charge matters! The charge state significantly influences the conformation and the binding energy between vancomycin antibiotic and bacterial cell-wall analogue peptides (see figure). Surface-induced dissociation (SID) studies provide a quantitative comparison between the stabilities of different charge states of the complex.



A review of the polycyclization reaction of the C$_{35}$ polyprenoid by squalene-hopene cyclase: Surprisingly, our results completely disagree with a previous publication in which it was reported that a hexacyclic skeleton was constructed as the single product. In our work many tri- and tetracyclic scaffolds were isolated, but no penta- or hexacycles. The reasons for the different results and the mechanism of the polycyclization reaction are discussed (see figure).

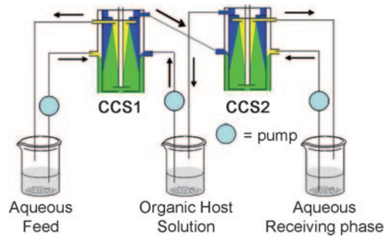
Coupling Reactions

On the tube: The coupling of diazonium ions onto single-walled carbon nanotubes is shown to proceed through a radical chain reaction by kinetic analysis of the absorption peak drop (see picture). Radical species are also revealed by ESR. Metallic (m) nanotubes play a special catalytic role in the functionalization of semiconducting (sc) nanotubes.

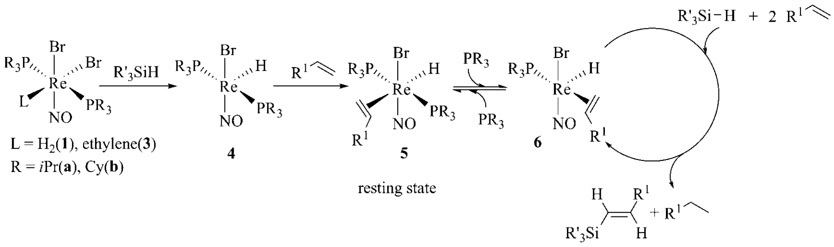


Continuous Separation

Resolution through revolution: It is possible to extract 3,5-dinitrobenzoyl-protected amino acids enantioselectively with the aid of a table-top centrifugal contact separator and a catalytic amount of a chiral host compound based on the Cinchona alkaloids. Enantioselectivities of up to 80 % could be reached in a single pass. This allows the development of a process for the continuous separation of racemates.



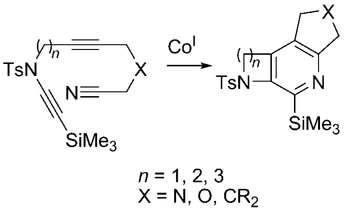
Homogeneous Catalysis



Choosy chemicals: Rhenium(I) complexes of type $[ReBr_2(L)(NO)(PR_3)_2]$ (L = H_2 (**1**), CH_3CN (**2**), ethylene (**3**); R = *i*Pr (**a**), cyclohexyl (**b**)) proved to be suitable catalyst precursors for the highly selective dehydrogenative silylation of alkenes. Two types of rhenium(I) hydride species, $[ReBrH(NO)(PR_3)_2]$ (**4**) and $[ReBr(\eta^2\text{-}CH_2{=}CHR^1)H(NO)(PR_3)_2]$ (**5**), were found in the $[ReBr_2(L)(NO)(PR_3)_2]$-catalyzed dehydrogenative silylation of alkenes.

Cycloaddition

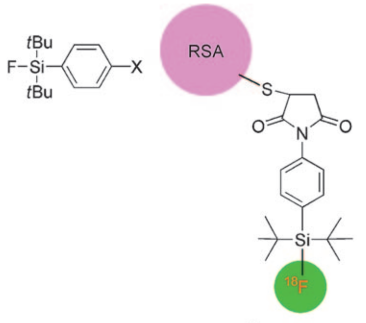
Three-ring circus: An expedient route to tricyclic fused 2-trimethylsilyl-3-aminopyridines exhibiting unprecedented skeletons is described. The key step is a very efficient cobalt-catalyzed [2+2+2] cycloaddition of a polyunsaturated compound displaying an ynamide, an alkyne, and a nitrile functionality (see picture).



Radiopharmaceuticals

*L. Iovkova, B. Wängler,**
E. Schirrmacher, R. Schirrmacher,
G. Quandt, G. Boening,
M. Schürmann,
*K. Jurkschat** 2140–2147

para-Functionalized Aryl-di-tert-butylfluorosilanes as Potential Labeling Synthons for ^{18}F Radiopharmaceuticals



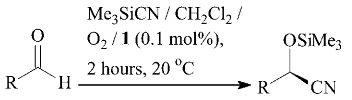
[^{18}F]SiFA-RSA

Broad spectrum: Novel *para*-functionalized aryl-di-*tert*-butylfluorosilanes, *p*-(tBu$_2$FSi)C$_6$H$_4$X (X = functional group), have been made available and broaden the spectrum of silicon-based ^{18}F acceptors (SiFAs) for potential PET applications. For example, the [^{18}F]maleimido derivative **1** has been employed for the synthesis of [^{18}F]**1**-labeled rat serum albumin (RSA), the applicability of which for PET has been verified by in vivo experiments.

Asymmetric Catalysis

Y. N. Belokon, W. Clegg,
R. W. Harrington, V. I. Maleev,
M. North, M. O. Pujol, D. L. Usanov,*
C. Young 2148–2165

Mechanism-Guided Development of VO(salen)X Complexes as Catalysts for the Asymmetric Synthesis of Cyanohydrin Trimethylsilyl Ethers



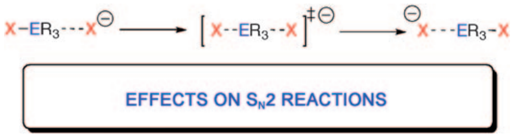
1 = VO(salen)NCS
salen = *N,N'*-(3,5-di-*tert*-butylsalicylidene)-(*S,S*)-1,2-diaminocyclohexane

Catalyze this! Detailed study of the mechanism of asymmetric cyanohydrin synthesis catalyzed by VO(salen)X complexes (see figure) led to the development of VO(salen)NCS, as the most active vanadium-based catalyst yet developed for this reaction.

Nucleophilic Substitution

I. Fernández, G. Frenking,**
*E. Uggerud** 2166–2175

The Interplay between Steric and Electronic Effects in S$_N$2 Reactions

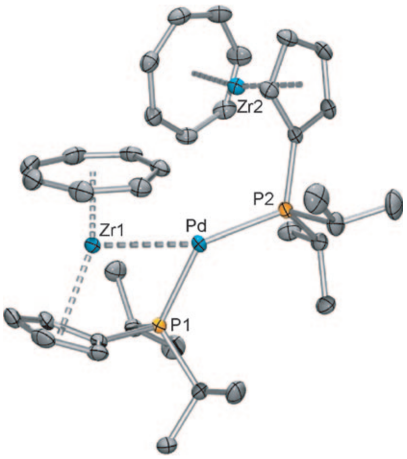


Myths of steric hindrance: In contrast with current opinion, energy decomposition analysis shows that the presence of bulky substituents at carbon leads to the release of steric repulsion in the transition state shown in the graphic. It is rather the weakening of the electrostatic attraction, and in particular the loss of attractive orbital interactions, that are responsible for the activation barrier.

Organometallic Chemistry

S. Büschel, A.-K. Jungton,
T. Bannenberg, S. Randoll, C. G. Hrib,
*P. G. Jones, M. Tamm** 2176–2184

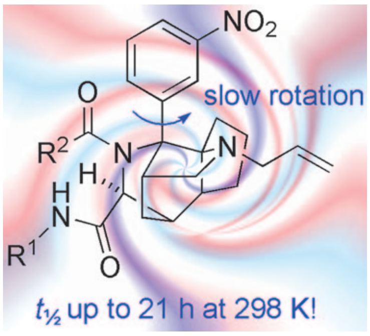
Secondary Interactions in Phosphane-Functionalized Group 4 Cycloheptatrienyl–Cyclopentadienyl Sandwich Complexes



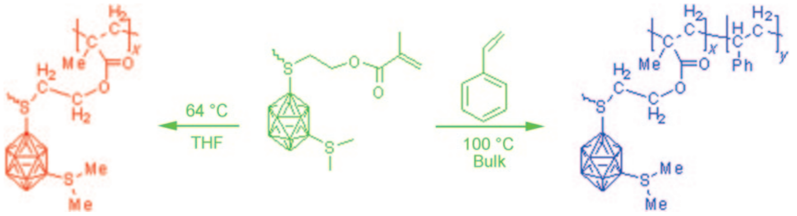
Twice as reactive: The coordination chemistry of phosphane-functionalized Zr and Hf cycloheptatrienyl–cyclopentadienyl complexes gives rise to unusual secondary interactions associated with the presence of Lewis acidic 16-electron sandwich moieties. These structures can develop weak dative bonds as exemplified by the noncovalent Pd→Zr interaction in the heterobimetallic {Zr$_2$Pd} complex (see picture).

Bond Rotation

Look, no *ortho* substituents! A series of polycycles were prepared by using a three-component Joullié–Ugi reaction. The rate of rotation about the bond between a highly hindered bridgehead and a phenyl ring with no *ortho* substituents was measured, and was highly dependent on the substitution. Rotamer half-lives of up to 21 h at 298 K were observed (see figure). Rotamers resulting from this restricted rotation were isolated for the first time.

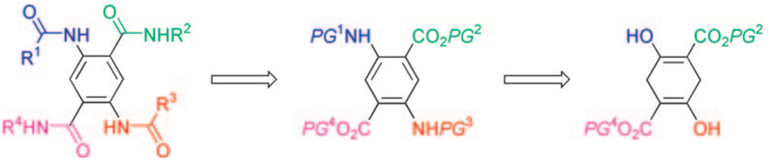


Inorganic Polymers



Chains of cages: Neutral/ionic $[B_{12}H_{12}]^{2-}$ boron-cage-functionalized methacrylate and styrene homopolymers or copolymers (see picture) are non-crystalline solids, T_g increases as the number of B_{12} cages in the chain of polystyrene increases, and homopolymers retain more weight than the copolymers when heated to 400 °C.

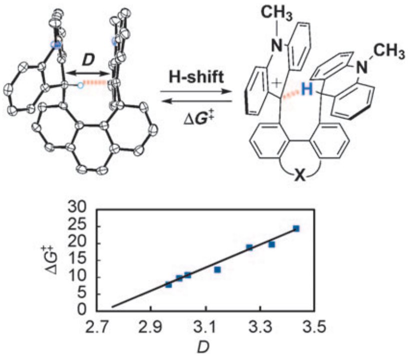
Peptide Coupling

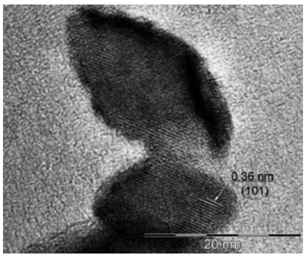


Fluorescent building blocks: Tetracarboxyamides with a central fluorescent diaminoterephthalate unit were prepared from succinyl succinates following a combinatorial-like strategy. The 2,5-diaminoterephthalates (see scheme; PG = protecting group) possess four points of diversification and are introduced as new scaffolds for combinatorial chemistry.

Carbocations

Bridging the gap: Snapshots of 1,6-H-shift precursors indicate that a narrower C–H···C$^+$ separation (*D* in the ORTEP diagram) in the title complexes induces faster degenerate rearrangement of **1**$^+$. A contact distance of less than 2.7 Å is necessary to realize the organic three-center two-electron bond of $[C-H-C]^+$, as indicated by extrapolation of the X-ray data.





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