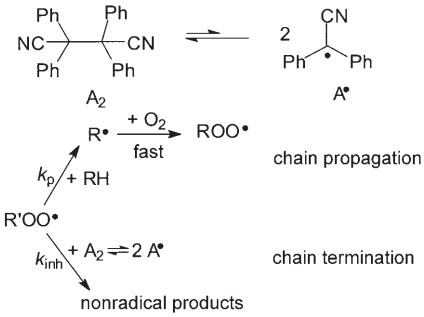
The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

Meeting Reviews

Books

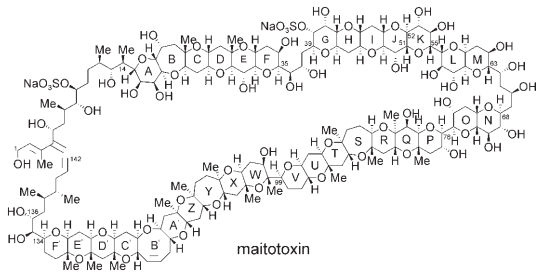
Highlights

Radical antioxidants: Carbon-centered radicals, which exist in thermal equilibrium with their dimers in solution, show unexpectedly low reactivity with molecular oxygen. Nevertheless their high reactivity with peroxyl radicals makes them a promising new class of chain-breaking antioxidants (see scheme).



C Radicals

Essays

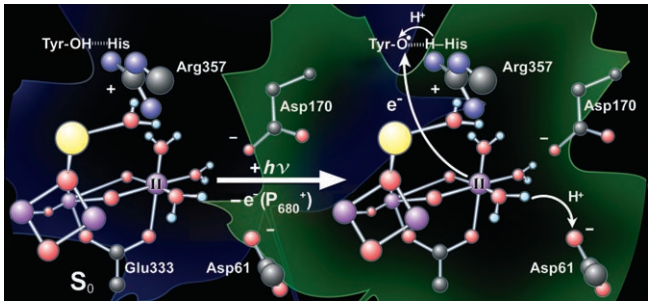


The right way round? Biosynthetic considerations have put the reported structure of maitotoxin in doubt, in particular the stereochemistry of its J/K ring junction (C51/C52, see structure). Further considerations on the basis of computational techniques lead, however, to the conclusion that the originally proposed structure is most likely correct.

Structure Elucidation

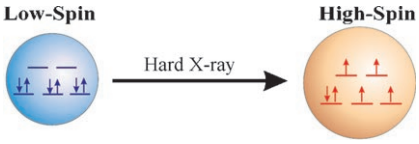
Contents

Reviews



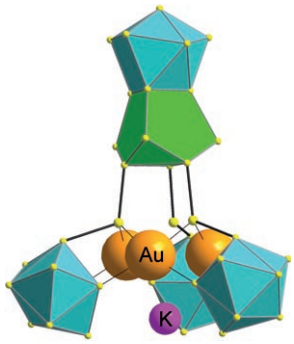
Wired for protons: The absorption of light in green plants by photosystem II results in oxidation of water to oxygen at the oxygen-evolving complex (OEC). It is now possible to suggest an important role for proton-coupled electron transfer in this mechanism (see picture). Crucial overall in a complex sequence of reactions is a combination of coupled electron–proton transfer and long-range proton transfer by sequential local proton transfers.

Communications



All Xcited: At low temperatures, an intense beam of hard X-rays excites photoswitchable molecular spin-crossover systems to generate metastable high-spin states (see picture). These states have spectroscopic properties similar to those of the states generated by light-induced excited-spin-state trapping. The new approach offers an excitation source with greater penetration.

The golden era of germanium: The largest known germanium cluster $[Au_3Ge_{45}]^{9-}$ consists of 45 Ge atoms coordinated to three Au atoms and is obtained by the reaction of K_4Ge_9 and $[AuCl(PPh_3)]$. DFT calculations reveal the large variety of chemical-bond character in the $\{Ge_{45}\}$ moiety; localized two-center, two-electron bonds coexist with delocalized polyhedral and three-center, two-electron bonds.



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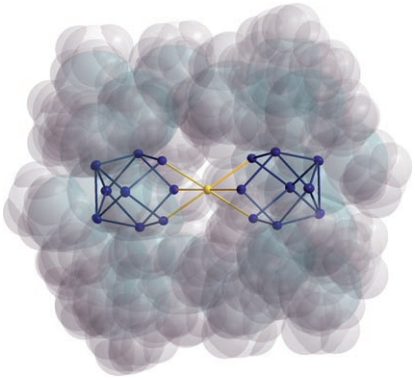
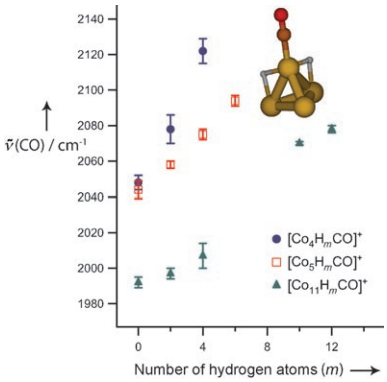
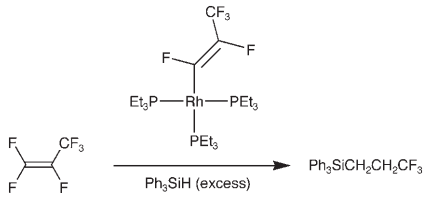


Well-protected: The first successful reaction with a metalloid cluster compound of Group 14 provides the new cluster species $[AuGe_{18}\{Si(SiMe_3)_3\}_6]^-$ (see picture; Ge blue, Au yellow, $Si(SiMe_3)_3$ groups are shown as a faded space-filling model), which can be considered as a first element on the way to a molecular cable.

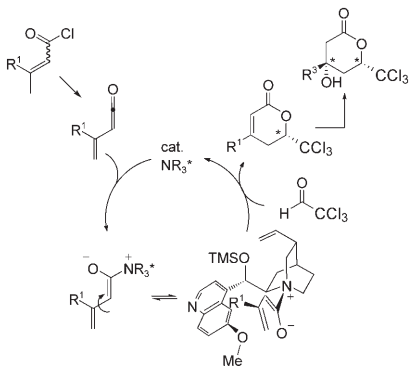
H in control (of the electrons): The bond strength of CO on small cationic cobalt clusters, as indicated by the C–O stretching band in the IR spectrum, can be precisely controlled by coadsorption of H_2 molecules. Each coadsorbed H atom reduces the electron density available for back-donation by about 0.09–0.25 electrons, depending on cluster size.



A clean break: The novel catalytic conversion of hexafluoropropene into (3,3,3-trifluoropropyl)silanes by C–F activation has been developed (see scheme). The reactions are catalyzed by the rhodium complex $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$, proceed at room temperature, and are highly selective.



Smooth elaboration: Versatile δ-lactone building blocks are provided by tertiary-amine-catalyzed asymmetric [4+2] cycloadditions of α,β-unsaturated acid chlorides and the electron-poor aldehyde chloral (see scheme). Silyl-substituted acid chlorides ($R^1 = R_3Si$) can be used for the diastereoselective synthesis of β-hydroxy-δ-lactones possessing quaternary stereocenters.



Incredibly inexpensive!

Do chemistry journals really cost so much? Perhaps some do, but certainly not *Angewandte Chemie*! In 2007, an entire institution could subscribe through Wiley InterScience for about 4200 Euro and get access to 48 issues with over 1600 articles and all associated online search options, and for just 10% more, the printed issues could be included as well. For full members of the German Chemical Society (GDCh), a personal subscription cost less than 300 Euro, and student GDCh members paid only 140 Euro, which is just under 3 Euro per issue – a price that even compares with high-circulation newsstand publications!

GDCh Gesellschaft Deutscher Chemiker

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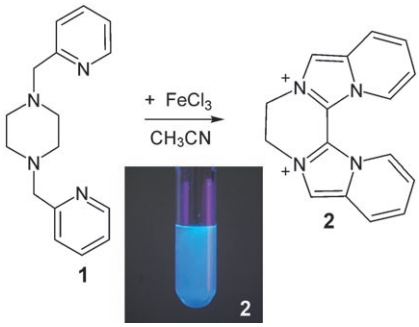
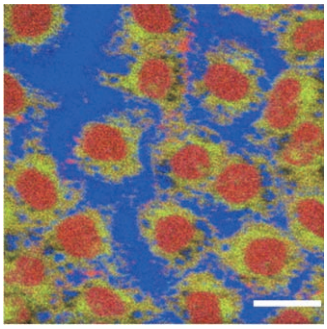
When having the blues isn't so bad: While normal coordination chemistry is observed when $FeCl_3$ and the potential ligand **1** (see scheme) are mixed in dichloromethane, redox chemistry occurs in acetonitrile, which involves C–H activation and C–N bond formation, and finally leads to a water-soluble blue fluorophore **2**.

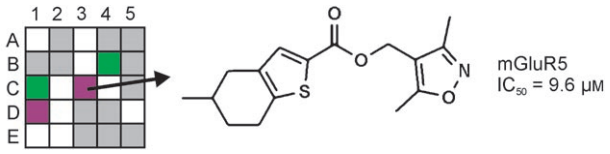


Oxidations



A peek inside: A C_{60}^+ sputter ion source integrated into a time-of-flight secondary-ion mass spectrometer was used to dissect animal cells in a layer-by-layer fashion and analyze the spatial distribution of endogenous molecules. Repeated cycles of sputter erosion and SIMS analysis provided molecular information from the inside of the cells (see picture; red: amino acids, green: phospholipids, blue: glass substrate).

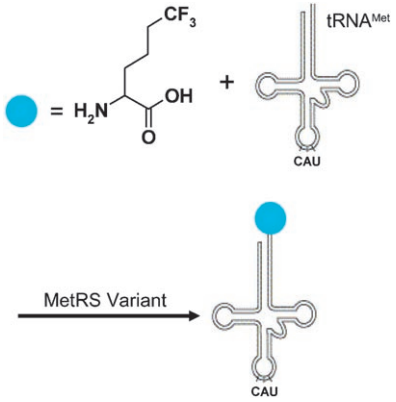
Mass Spectrometry



No longer lost in space: A virtual screening approach for the mapping of chemical space using supervised and unsupervised neural networks is presented. Novel scaffolds of allosteric antagonists for mGluR 5 were identified in regions of chemical space that were not covered by active molecules from the training set.

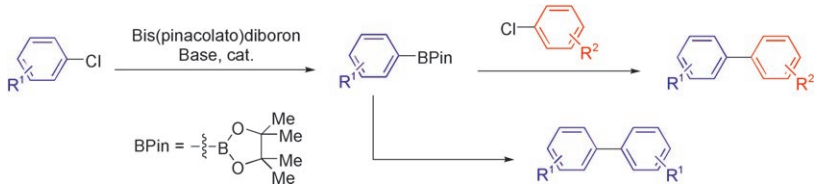
Virtual Screening

A change for the better: An efficient method for the identification of mutant methionyl-tRNA synthetases (MetRS) has been developed that enables global incorporation of noncanonical amino acids into recombinant proteins. By using the method, an MetRS variant has been identified that enables near-quantitative replacement of methionine by 6,6,6-trifluoronorleucine (see scheme).



Protein Engineering

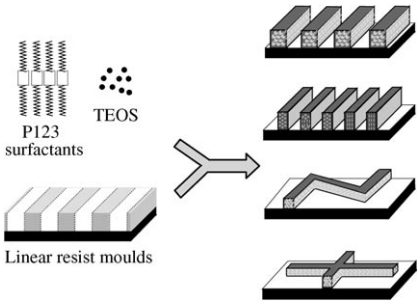
Contents



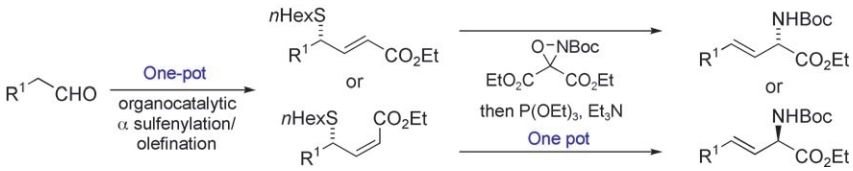
From chloride to boronate: Catalysts comprising palladium and biaryl monophosphine ligands provide highly active systems for the borylation of aryl and heteroaryl chlorides (see scheme). Symmetrical and unsymmetrical biaryl products can also be prepared directly from two aryl chlorides without isolation of the intermediate boronate esters. Computational studies provide insight into the roles of the biaryl phosphine ligand and the KOAc base in the catalytic cycle.

C–C Coupling

A top-down/bottom-up approach has been developed to fabricate mesoporous silica with well-aligned mesochannels of controlled orientation by means of cooperative assembly of an amphiphilic triblock copolymer (P123) and silica species within lithographically designed confined nanospaces. Some mesochannel patterns that can be prepared by this technique are shown schematically in the picture. TEOS = tetraethoxysilane.

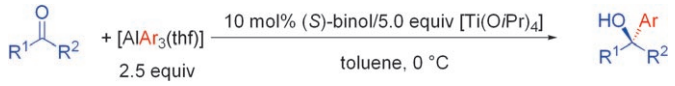


Mesoporous Materials



Have it both ways: Enantiomerically enriched *E* vinyl glycines may be accessed from aldehydes in a concise sequence that combines an organocatalytic α sulfenylation, stereoselective olefination, a sulfimidation, and a [2,3] sigmatropic rearrangement (see scheme, Boc = *tert*-butoxycarbonyl, *n*Hex = *n*-hexyl). Either enantiomeric series can be accessed by control of the alkene geometry in the olefination step.

Asymmetric Synthesis

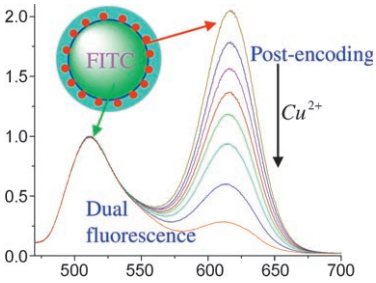


Chiral transfer: Novel asymmetric aryl transfers from [$AlAr_3$(thf)] to a wide variety of ketones are catalyzed by an in situ generated titanium species with (*S*)-binol as the chiral ligand. The reaction affords tertiary alcohols with enantioselectivities up to 97% *ee* (see scheme). Binol = 2,2′-dihydroxy-1,1′-binaphthyl.

Asymmetric Arylation

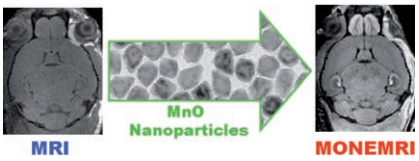
Contents

Dual control: Hybrid silica–nanocrystal–organic dye superstructures comprising fluorescein isothiocyanate (FITC)-doped silica cores, embedded CdTe quantum dots, and an outer silica shell display well-resolved dual fluorescence emission. Multicolor encoding fluorescent probes are generated by modulating the fluorescence intensity ratio of the dual emission by a simple post-encoding strategy (see picture).

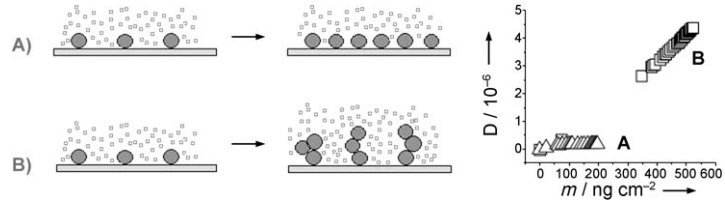


Fluorescent Probes

Contrasting images: A new T_1 contrast agent for magnetic resonance imaging (MRI) based on MnO nanoparticles reveals a bright signal enhancement and fine anatomic structures in the T_1-weighted MR image of a mouse brain (see picture; left MRI, right MnO-enhanced MRI (MONEMRI)). Furthermore, MnO nanoparticles conjugated with a tumor-specific antibody were used for selectively imaging breast cancer cells in a metastatic tumor in brain.



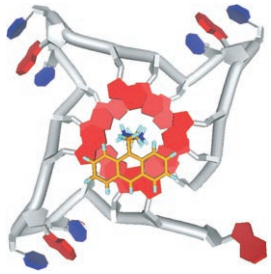
Imaging Agents



Covering up: The greater ability of antifreeze proteins (AFPs), relative to polyvinyl pyrrolidone (PVP), to inhibit the reformation of gas hydrates, despite their smaller adsorption mass, has been explained by using a quartz crystal microbalance equipped with the ability to measure the dissipation factor (D). Whereas AFPs can form a rigid and compact film on the nucleating surface (A), PVP forms a porous and loose film (B).

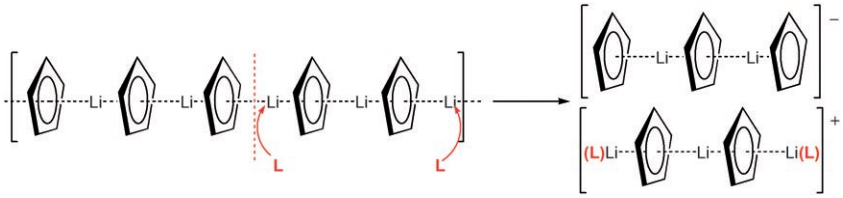
Surface Chemistry

Under control: An anthracene polyammonium derivative induces folding of the highly polymorphic human telomeric DNA into a single parallel G-quadruplex conformer through an unusual mode of interaction. The sequential use of this ligand and a porphyrazine allows controlled conformational switching of the quadruplex between parallel and antiparallel conformations.



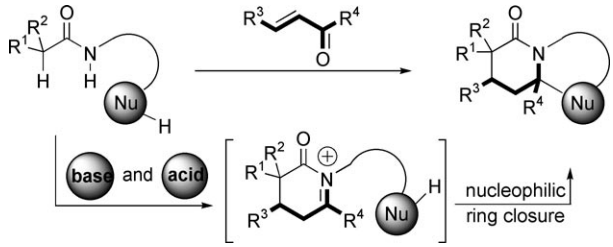
DNA Folding

Contents



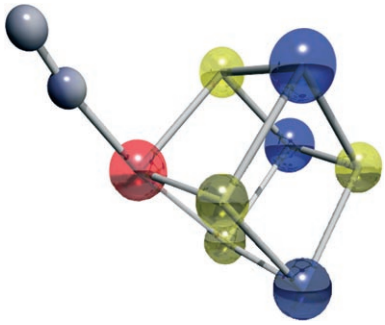
Breaking up: The first triple-decker sandwich anion $[(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})]^-$ of lithocene ($\text{Cp} = \text{C}_5\text{H}_5$) (observed in the charge-separated complex $[(\mathbf{L})\text{Li}(\mu\text{-Cp})\text{Li}(\mu\text{-Cp})\text{Li}(\mathbf{L})]^+[(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})\text{Li}(\eta^5\text{-Cp})]^-$) is formed in the reaction of $[\text{Cp}_2\text{V}]$ with hppLi (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine). The V≡V-bonded complex $[\text{V}_2(\text{hpp})_4]$ (**L**) effectively acts as a ligand to intercept the polymeric structure of $[\text{CpLi}]_\infty$ (see scheme).

Cyclopentadienyl Ligands



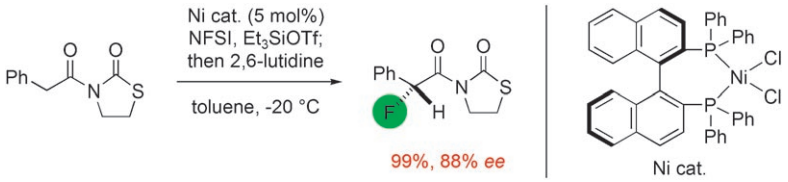
One thing leads to another: Site-isolated base and acid catalysts have been exploited in Michael addition, *N*-acyl iminium ion cyclization cascades with amide pronucleophiles and α,β-unsaturated carbonyl compounds. The reaction sequence has broad scope, uses commercially available catalysts, is atom efficient, and can be scaled by way of a flow-reactor setup.

Michael Addition



An end-on N_2 ligand is the outstanding feature in $[\{\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\}_3\{\text{Ru}(\text{tmeda})(\text{N}_2)\}(\mu_3\text{-S})_4]$ ($\text{tmeda} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), the first cubane-type metal sulfido cluster with a dinitrogen ligand, which has been isolated and fully characterized by single-crystal X-ray analysis. The picture shows the cluster core with the Ru-bound N_2 ligand (Ir blue, N gray, Ru red, S yellowish green).

Nitrogen Fixation

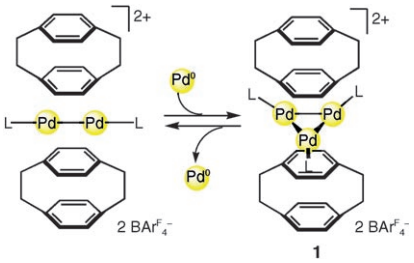


Not binary, but trinary: A binary system consisting of $\text{Ni}(\text{OTf})_2$–binap complex and 2,6-lutidine failed to promote the asymmetric fluorination of ester equivalents. However, upon the addition of a substoichiometric amount of Et_3SiOTf to the NiCl_2–binap/2,6-lutidine catalyst, the monofluorinated products were obtained in good yield with high enantioselectivity (see example). NFSI = *N*-fluorobenzenesulfonimide, Tf = trifluoromethanesulfonyl.

Asymmetric Catalysis

Contents

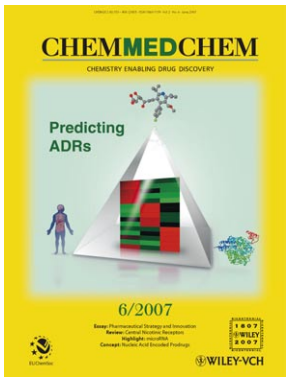
Sandwich triangles: A bis([2.2]paracyclophane)tripalladium complex (**1**) was isolated and characterized by NMR spectroscopy, and a mixed-ligand derivative was structurally characterized. These complexes are the first isolated μ_3-arene trimetal complexes of a Group 10 metal. Complex **1** undergoes facile release of a Pd^0 atom (see scheme) and as such may be regarded as a Pd^0 reservoir.



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

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

Service



For more information on ChemMedChem see www.chemmedchem.org

Corrigenda

The concentrations of peptide used in the studies in this Communication were incorrectly quoted. All Aβ concentrations should be multiplied by a factor of 10; that is, $[Cu^{2+}]/[A\beta] = 1$, 4, and 6 (instead of 0.1, 0.4, and 0.6, respectively). The authors apologize for the oversight but point out that the ESR and TEM results still demonstrate a correlation between the specific Cu^{2+} ion coordination and the overall morphology of aggregates.

The Aggregated State of Amyloid-β Peptide In Vitro Depends on Cu^{2+} Ion Concentration

S. Jun, S. Saxena* ——— **3959–3961**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200700318

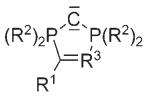
In this Communication, the substituent labels for P-heterocyclic carbodiphosphoranes **2** (Scheme 2) were incorrectly shown and incorrectly listed in Table 1 for the proton affinities. The correct structure of **2** is shown below, along with the revised part of Table 1 corresponding to **2**. The authors apologize for the oversight but point out that their conclusions are not affected by this error.

Carbodiphosphoranes: The Chemistry of Divalent Carbon(0)

R. Tonner, F. Öxler, B. Neumüller,* W. Petz,* G. Frenking* ——— **8038–8042**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200602552



2

Table 1: Calculated (RI-MP2/TZVPP//RI-BP86/SVP) first and second proton affinities (PAs) in kcal mol^{-1}.

	P-heterocyclic CDPs			1st PA	2nd PA
	R^1	R^3	R^2		
2a	H	N	H	251.5	110.5
2b	H	N	Me	270.8	143.3
2c	H	N	NH_2	271.4	138.1
2d	H	N	NMe_2	275.3	157.8
2e	Me	N	NMe_2	277.6	160.3
2f	Ph	N	$NiPr_2$	284.2	188.3
2g	Ph	N	$NiPr_2$, $iPr_2N(CH_2)_2NiPr_2$	284.5	179.0
	R^2	R^3	R^1		
2h	H	CH	H	261.8	119.1
2i	H	CH	Me	278.2	149.7
2k	H	CH	NH_2	277.5	144.6
2l	H	CH	NMe_2	280.0	162.6
2m	Me	CH	$NiPr_2$	287.3	190.5

Retraction

After the online publication of this Communication (March 30, 2007), it has been brought to the authors' attention that the ^{13}C NMR spectra of the assumed azepinoazepine synthesized are essentially identical to those of the viologen structure.[1] ^1H NMR spectra also support this finding, although they were measured in different solvents and at different field strengths.[2] The authors therefore retract this Communication and apologize for any inconvenience.

Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines

I. Yamaguchi,* S. Tsutsui, M. Sato

DOI 10.1002/anie.200700170

[1] W. W. Porter III, T. P. Vaid, *J. Org. Chem.* **2005**, *70*, 5028.
[2] H. Kamogawa, S. Sato, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 321.

Nitrogen Heterocycles

DOI: 10.1002/anie.200700170

Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines**

Isao Yamaguchi, Saori Tsutsui, and Moriyuki Sato*

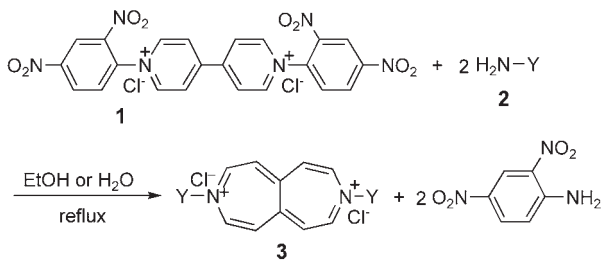
Azepine derivatives fused with aromatic rings represent an important class of compounds as they display potential or proven pharmacologic activity.[1] A large number of reports on synthetic approaches towards these compounds have been published.[2] Metal-complex-catalyzed intramolecular cyclization reactions are useful for the synthesis of azepine derivatives fused with aromatic rings such as benzene, imidazole, and pyridine rings.[3] However, these cyclization reactions sometimes cause undesirable side reactions. Ring-expansion reactions are also utilized for the preparation of azepine derivatives, and they proceed without side reactions.[4] It has been reported that the photolysis of diazidonaphthalenes causes ring expansion to yield azepinoazepines.[4d] These azepinoazepines are not fully unsaturated, and attempts to convert them into fully unsaturated diazaheptalene have been unsuccessful. Fully unsaturated azepinoazepine should show interesting optical and electrochemical properties as a result of its π-conjugated electron system. To the best of our knowledge, there has been only one report on the azepinoazepines[4d] and fully unsaturated azepinoazepines have not been prepared so far.

Recently, we reported the ring expansion of the pyridyl group of *N*-(2,4-dinitrophenyl)pyridinium chloride into diaza[12]annulene by reaction with an amine.[5] According to this reaction, the reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**) with an amine may provide a diaza[12]annulene dimer. However, we found that the reaction yields unexpected products, namely N-substituted azepinoazepines. These products are a new type of azepine derivative with an expanded π-conjugation system.

Organic reactions in aqueous media have received considerable attention because of their potential advantages with regard to costs, safety, and environmental concerns.[6] In contrast to many reports on organic reactions in mixtures of water and organic solvents, organic syntheses in water, except for simple hydrolysis reactions, are limited as a result of the poor solubility of organic reactants in water. Compound **1** and certain amines used as starting materials in this work are soluble in water, and the previously reported reaction of water-soluble *N*-(2,4-dinitorophenyl)pyridinium chloride with amines proceeds smoothly in water to provide N-substituted diaza[12]annulene through ring expansion of the pyridyl group. These results urged us to carry out the reaction of **1** with amines in water.

Herein, we report the results of the reaction of **1** with various amines **2** in ethanol and water, as well as the structures and optical and electrochemical properties of the obtained azepinoazepines **3**. A plausible reaction pathway is also proposed.

Reaction of **1** with substituted amines **2** (1:2) in refluxing EtOH (Scheme 1) gave rise to N-substituted azepinoazepine dichlorides **3**. Use of water-soluble amines **2a**–**2d** under aqueous conditions also yielded the azepinoazepines **3a**–**3d**. The results of these reactions are summarized in Table 1. The obtained azepinoazepines **3** were soluble in water and in organic solvents such as methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Their structures were determined by FAB mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis.



Scheme 1. Reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**) with amines **2**. See Table 1 for Y groups.

Figure 1 depicts the ^{1}H NMR spectra of **3d**–**3g** in D_2O. Peaks at approximately $\delta = 9.3$ and 8.7 ppm are assigned to H^a and H^b of the azepinoazepine ring, respectively. The observation of the two signals of the azepinoazepine ring suggests that π electrons are delocalized along the azepinoazepine ring, as shown in Figure 1. ^{13}C NMR spectroscopy data also support this view, showing three signals attributed to the azepinoazepine ring.[7] The ^{1}H NMR peak positions of the azepinoazepine ring of **3a**–**3h** are essentially the same, independent of the structure of the N substituents. The difference in the chemical shifts between the two halophenyl hydrogen atoms H^c and H^d of **3d**, **3f**, and **3g** are $\delta = 0.38$, 0.11, and 0.57 ppm, respectively, whereas the two signals of chlorophenyl hydrogen atoms of **3e** are located at essentially the same position. These data suggest that the azepinoazepine

[*] Prof. Dr. I. Yamaguchi, S. Tsutsui, Prof. Dr. M. Sato
Department of Material Science
Faculty of Science and Engineering
Shimane University
1060 Nishikawatsu, Matsue 690-8504 (Japan)
Fax: (+81) 852-32-6421
E-mail: iyamaguchi@riko.shimane-u.ac.jp

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Table 1: Reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride **1** with amines **2**.[a]

Entry	Y (amine)	**2**	Solvent	Product	Yield [%][b]
1	C_6H_5	**2a**	EtOH	**3a**	91
2			H_2O		75
3	4-$MeOC_6H_4$	**2b**	EtOH	**3b**	90
4			H_2O		69
5	2,5-$Me_2C_6H_3$	**2c**	EtOH	**3c**	84
6			H_2O		45
7	4-FC_6H_4	**2d**	EtOH	**3d**	91
8			H_2O		71
9	4-ClC_6H_4	**2e**	EtOH	**3e**	78
10	4-BrC_6H_4	**2f**	EtOH	**3f**	88
11	4-IC_6H_4	**2g**	EtOH	**3g**	84
12	*p*-terphenyl	**2h**	EtOH	**3h**	95
13	*n*-hexyl	**2i**	EtOH	**3i**	38

[a] A solution of **1** and **2** in 1:2 molar ratio in either ethanol (entries 1, 3, 5, 7, and 9–13) or water (entries 2, 4, 6, and 8) was heated at reflux for 12 h under nitrogen (see Scheme 1 for details). [b] Yield of isolated product.

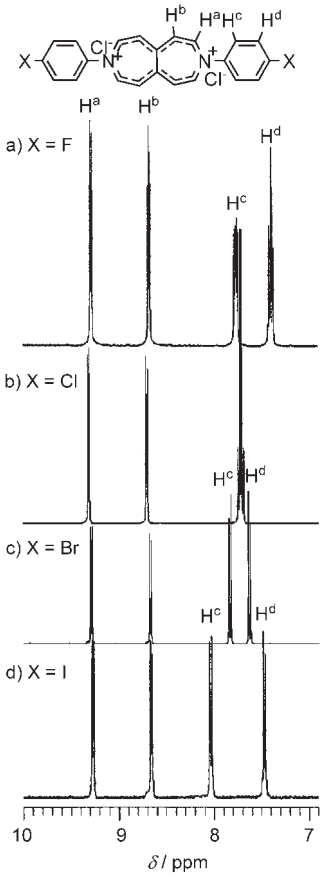


Figure 1. ^{1}H NMR spectra of **3d**–**3g** in D_2O.

ring has an electron-withdrawing property similar to that of the chloro group.

The absorption peaks of **3** are influenced by the structures of the N substituents, as summarized in Table 2. Azepinoazepine dichloride **3h** with *p*-terphenyl substituents shows absorptions at longer wavelengths as compared to the other azepinoazepines, and the absorptions of **3i** with non-aromatic substituents lie at the shortest wavelength among the azepinoazepine dichlorides. These data suggest that the π-conjugation system is expanded from the azepinoazepine ring to the aromatic N substituents. The observation of the absorption of **3b** at a wavelength longer than that of **3c** is explained by the steric effect of the methyl group at the 2-position of the 2,5-dimethylphenyl ring that may hinder the expansion of the π-conjugation system.

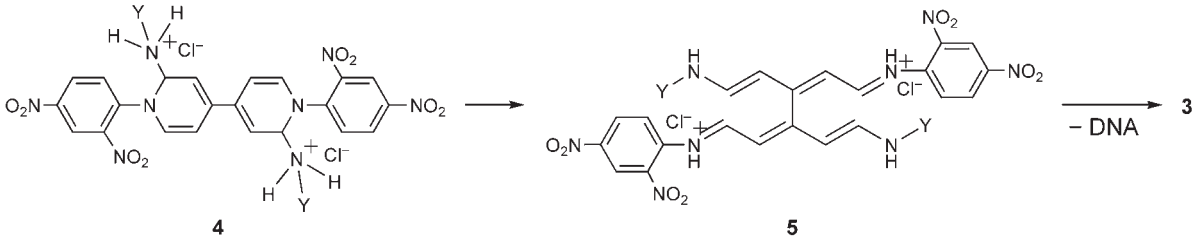
Table 2: Absorption and electrochemical data for azepinoazepines **3**.

Entry	**3**	λ_{max}[a] [nm] ($\log\varepsilon$)	$E_{pc}(1), E_{pc}(2)$ [V][b]	$E_{pa}(1), E_{pa}(2)$ [V][b]
1	**3a**	245 (4.11), 320 (4.49)	−1.53	−0.48, 0
2	**3b**	253 (4.26), 380 (4.67)	−1.51	−0.84, −0.45
3	**3c**	255 (4.05), 268 (4.07), 299 (3.97)	−1.84	−0.92, −0.44
4	**3d**	255 (4.02), 299 (4.09), 321 (4.08)	−1.48	−0.57, −0.05
5	**3e**	259 (4.12), 290 (4.13), 326 (4.16)	−1.23, −1.74	−1.10, −0.61
6	**3f**	254 (4.05), 329 (4.19)	−1.17, −1.73	−1.11, −0.13
7	**3g**	240 (4.07), 342 (4.27)	−1.06, −1.88	−0.15
8	**3h**	289 (4.35), 385 (3.99)	−1.47	−0.88, −0.31
9	**3i**	261 (≈3.8)	−2.02	−1.75, −1.19

[a] Absorption in ethanol. [b] Film cast on a Pt plate, measured in a CH_2Cl_2 solution of $(Et_4N)BF_4$ (0.1 M). The sweep rate was 50 mVs^{-1}. E_{pc} = Peak cathode potential versus Ag^+/Ag. E_{pa} = Peak anode potential versus Ag^+/Ag.

Cyclic voltammetry measurements suggested that the film of the azepinoazepines cast on a Pt plate underwent two-step electrochemical reduction of the azepinoazepine ring in a dichloromethane solution containing 0.1M $(NEt_4)BF_4$. The electrochemical data also are summarized in Table 2. Azepinoazepines **3e**–**3g** with N-halophenyl substituents showed two reduction peaks, which were coupled with anodic peaks $E_{pa}(1)$ and $E_{pa}(2)$. Although the peaks attributed to the two-step electrochemical reduction of the other azepinoazepines **3a**–**3d**, **3h**, and **3i** were duplicated, the two anodic peaks were separately observed. The reduction potential was dependent on the N substituent; product **3i** with its electron-donating *n*-hexyl substituents (Table 2, entry 9) showed a peak at higher reduction potential as compared to **3d**–**3g**, which have electron-withdrawing substituents (entries 4–7). The yellow film of the azepinoazepines changed to green after the electrochemical reduction and returned to yellow after crossing the $E_{pa}(2)$ peak.

Scheme 2 shows a plausible reaction mechanism for formation of the N-substituted azepinoazepine dichlorides. The nucleophilic addition of an amine to the pyridinium rings of **1** occurs first to provide the intermediate **4**. Subsequently, ring opening of the dihydropyridyl rings of **4** gives an



Scheme 2. Possible reaction mechanism for the formation of N-substituted azepinoazepine dichlorides **3**.

intermediate **5**, which undergoes cyclization by elimination of 2,4-dinitroaniline (DNA) to provide **3**.

The product from expansion of one pyridinium ring of **1** was not obtained. On the other hand, nucleophilic addition of the NH group of the intermediate **5** to **1** followed by ring opening of the dihydropyridyl ring and elimination of 2,4-dinitroaniline may yield N-substituted diaza[13]annulenoannulene tetrachloride. However, such a product is not formed in the reaction of **1** with **2** as the lower basicity of the NH group of the intermediate **5** prevents nucleophilic addition to the pyridinium ring. These results indicate that the nucleophilic addition of an amine to the pyridyl group is a crucial step for the generation of the azepinoazepine ring.

In conclusion, N-substituted azepinoazepines were obtained in high yields by the one-pot reaction of **1** with amines. ^{1}H NMR spectra of the products revealed that the π electrons are delocalized along the azepinoazepine ring. Cyclic voltammetry analysis indicated that the azepinoazepines are electrochemically active in films, and the electrochemical reaction was accompanied by electrochromism. Polymerization of **1** with aromatic diamines could provide π-conjugated polymers with the azepinoazepine ring in the main chain. In addition, the azepinoazepines **3d–3g** with 4-halophenyl substituents could be useful starting materials for functional compounds and polymers. These topics are currently under investigation in our laboratory.

Experimental Section

Representative procedure. Preparation of **3a** in EtOH (Table 1, entry 1): 1,1′-Bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride (**1**; 1.12 g, 2.0 mmol) and aniline (**2a**; 0.37 g, 4.0 mmol) were dissolved in dry ethanol (8 mL) under N_2. The solution was heated at reflux for 12 h under nitrogen, and then the brown precipitate from the reaction solution was separated by filtration. The precipitate was washed with acetone (150 mL) and dried under vacuum to give the title compound **3a** (0.59 g, 77%) as a brown solid. Compound **3a** was also obtained from the filtrate: Evaporation of the solvent from the filtrate gave a brown solid, which was washed with acetone (150 mL) and dried in vacuo to further afford compound **3a** (0.11 g, 14%). Total yield: 91%.

Preparation of **3a** in water (Table 1, entry 2): An aqueous solution (4 mL) of **1** (0.56 g, 1.0 mmol) and **2a** (0.19 g, 2.0 mmol) was heated at reflux for 12 h, and then the 2,4-dinitroaniline precipitated from the reaction solution was filtered. Evaporation of water gave a brown solid, which was washed with acetone (150 mL) and dried under vacuum to afford compound **3a** (0.29 g, 75%). ^{1}H NMR (400 MHz, D_2O): $\delta = 9.30$ (d, $J = 7.2$ Hz, 4H), 8.67 (d, $J = 7.2$ Hz, 4H), 7.63–7.73 ppm (m, 10H); ^{13}C{^{1}H} NMR (100 MHz, [D_6]DMSO): $\delta = 148.9$, 146.0, 142.2, 131.6, 130.2, 126.7, 124.8 ppm. FAB-MS: m/z 345 [$M-Cl^-$], 310 [$M-2Cl^-$]; elemental analysis (%) calcd for $C_{22}H_{18}N_2Cl_2 \cdot 1.5\,H_2O$: C 64.71, H 5.18, N 6.86; found: C 64.86, H 5.13, N 6.40.

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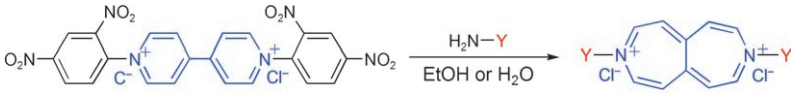
[7] See Supporting Information.

Communications

Nitrogen Heterocycles

I. Yamaguchi,* S. Tsutsui,
M. Sato ——— ▮▮▮▮–▮▮▮▮

Ring Expansion of a 4,4′-Bipyridyl Derivative into π-Conjugated Azepinoazepines



Room to expand: N-substituted azepinoazepines were obtained in high yields from 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride with amines. The ^{1}H NMR spectra of the products revealed that π electrons were delocalized along the azepinoazepine ring, while cyclic voltammetry analysis indicated that the azepinoazepines were electrochemically active and electrochromic as thin films.