ANGEWANDTE CHEMIE

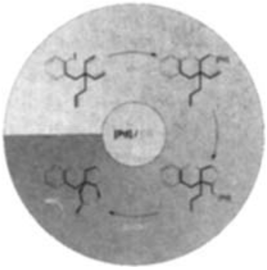
A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/18
Pages 2005–2160

COVER PICTURE

The cover picture shows the palladium-catalyzed cyclization cascade of an iodotriene in the presence of CO in which "living" organopalladium species are formed as intermediates. Remarkably, this reaction succeeds with terminal alkenes that usually undergo β-dehydropalladation in the Heck reaction. E. Negishi et al. report more about this first cascade-type acylpalladation yielding polycycles with an angular mode of fusion on p. 2125ff. In the reaction shown seven C–C bonds are formed in one step.



REVIEWS

Contents

Two and sometimes even three metal ions are essential for the activity of many enzymes that catalyze the hydrolysis of phosphate ester and amide bonds. In addition to many mononuclear metallohydrolases, a number of metalloenzymes have been structurally characterized in which the active sites contain two adjacent metal ions that permit the transfer of phosphoryl and acyl groups. These studies provide detailed insight into the chemistry of two-metal ion catalysis—an important step towards the design of new artificial catalysts.

N. Sträter, W. N. Lipscomb,*
T. Klabunde, B. Krebs* 2024–2055

Two-Metal Ion Catalysis in Enzymatic Acyl- and Phosphoryl-Transfer Reactions

---

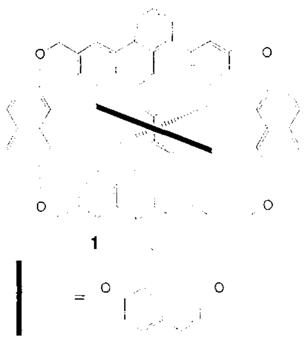
The efficiency of a demanding synthesis is often determined by the combination of protecting groups employed. Tried-and-true protecting groups are briefly presented here, including those that can be cleaved with acids, bases, fluoride ions, oxidation, reduction, light, and enzymes. Examples from published syntheses outline general themes and tactics for the development of successful protecting group strategies.

M. Schelhaas,
H. Waldmann* 2056–2083

Protecting Group Strategies in Organic Synthesis

HIGHLIGHTS

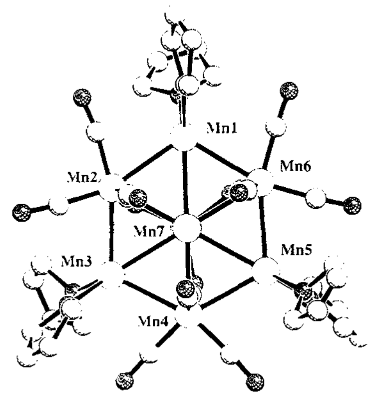
A cocktail of imaginative synthetic approaches, unique conformational behavior and analysis, unusual spectroscopic properties, and asymmetric synthesis, all liberally spiced with an assortment of intriguing structures (like **1**), is served up to illustrate recent advances in the diverse field of cyclophane chemistry. Cyclophanes can be auxiliaries in asymmetric synthesis and perhaps also starting materials for fullerenes.



G. J. Bodwell* 2085–2088

The New Inductees in the "Hall of Phane" No Phane, No Gain

Direct linkage of complex fragments of the classical Werner-type with metal carbonyl complex fragments characterizes a novel type of open-shell transition metal cluster, for which the term xenophilic has been proposed. These polynuclear complexes may display new metal frameworks with nonbridged metal–metal bonds; the structure of such a fragment ($[Mn_7(thf)_6(CO)_{12}]^-$) is depicted on the right.

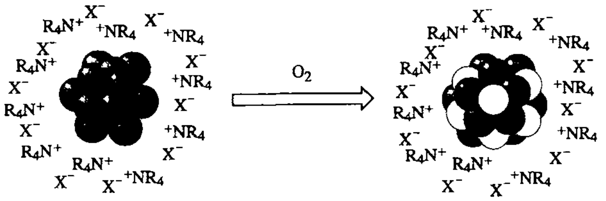


L. H. Gade* 2089–2090

"Strangelove" in Cluster Chemistry: A New Class of Open-Shell Transition Metal Clusters

COMMUNICATIONS

Complete oxidation without formation of bulk CoO results when cobalt clusters stabilized with $R_4N^+X^-$ are exposed to O_2. Since the resulting soluble, nanostructured cobalt(II) oxide clusters (idealized representation below; dark spheres: metal atoms; light spheres: oxygen atoms; $R = C_8H_{17}$) do not penetrate very far into the pores of Al_2O_3 pellets, unlike the Co clusters, these materials are potential shell catalysts.

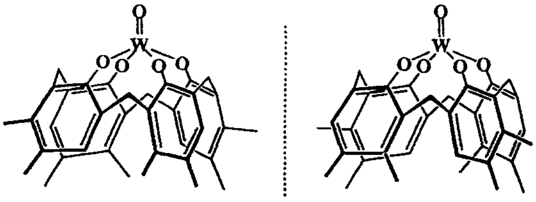


M. T. Reetz,* S. A. Quaiser, M. Winter, J. A. Becker, R. Schäfer, U. Stimming, A. Marmann, R. Vogel, T. Konno 2092–2094

Nanostructured Metal Oxide Clusters by Oxidation of Stabilized Metal Clusters with Air

---

Complexation with dichlorotungsten or oxotungsten groups locks chiral calix[4]arenes into rigid cone conformations. The resulting chiral metallocalix[4]arenes such as **1** (picture shows both enantiomers) have been resolved for the first time and are potential building blocks for new materials and supramolecular catalysts.

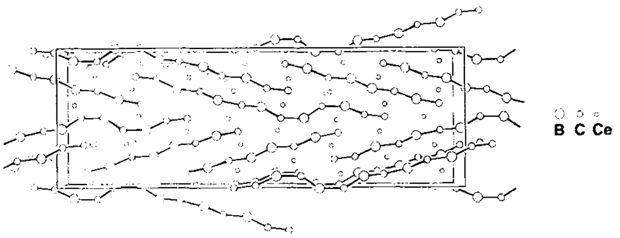


1

B. Xu, P. J. Carroll, T. M. Swager* 2094–2097

Chiral Metallocalix[4]arenes: Resolution by Diastereomeric Tungsten(VI) Alkoxides

B_xC_y cumulene-like chains with up to 13 atoms can be stabilized in compounds such as $Ce_{10}B_9C_{12}$ (see picture). In a first approximation the bonding between the metal and the nonmetal atoms can be considered as ionic (for instance, $(Ce^{1.7+})_{10}(B_4C_4)^{8-}(B_5C_8)^{9-}$).

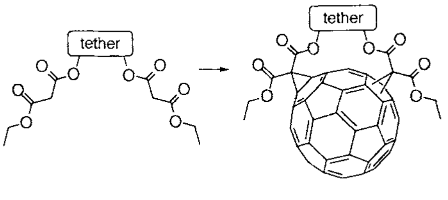


D. Ansel, J. Bauer,* F. Bonhomme,
G. Boucekkine, G. Frapper, P. Gougeon,
J.-F. Halet,* J.-Y. Saillard,*
B. Zouchoune 2098–2101

Boron–Carbon Chains Stabilized in Rare Earth Metallic Frameworks

---

A versatile and simple method provides access to covalent bisadducts of C_{60} with high regio- and diastereoselectivity. Starting from optically pure bis(malonate) derivatives and C_{60}, a double Bingel reaction afforded optically active *cis*-3 bisadducts (*ee* > 97%), whose chirality results exclusively from the addition pattern.

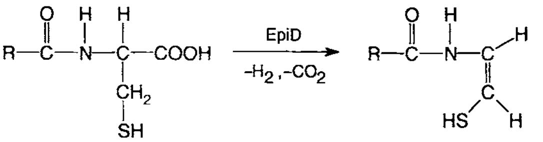


J.-F. Nierengarten, V. Gramlich,
F. Cardullo, F. Diederich* 2101–2103

Regio- and Diastereoselective Bisfunctionalization of C_{60} and Enantioselective Synthesis of a C_{60} Derivative with a Chiral Addition Pattern

---

A key player in the biosynthesis of epidermin, the novel enzyme EpiD converts peptidyl cysteines into thioenols [Eq. (a)]. The thioenols are unstable and decompose within hours. The oxidative decarboxylation of a ^{13}C-labeled peptide substrate was monitored by mass spectrometry and NMR spectroscopy, and the structure of the intermediate in the biosynthesis was determined. R = peptide residue.



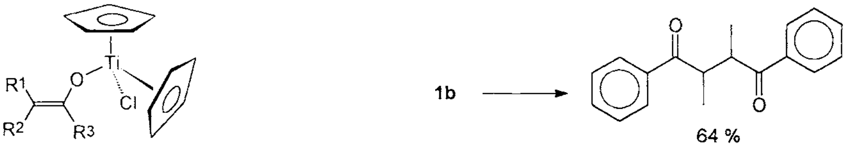
$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SH}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}}}{-}COOH \xrightarrow[-H_2,-CO_2]{EpiD} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}CH{=}CH{-}SH \qquad (a)$$

C. Kempter, T. Kupke, D. Kaiser,
J. W. Metzger, G. Jung* 2104–2107

Thioenols from Peptidyl Cysteines: Oxidative Decarboxylation of a ^{13}C-Labeled Substrate

---

Unusually stable against hydrolysis is the titanium enolate **1a** (R^1, R^2 = Mes, R^3 = H), which can be stored in air for three months without any decomposition and leads, after one-electron oxidation, to the first titanium enolate radical cation characterized in solution. These novel electrophiles undergo Ti–O bond cleavage and C–C bond formation, for example in the synthesis of **2** from titanium enolate **1b** (R^1 = H, R^2 = Me, R^3 = Ph).



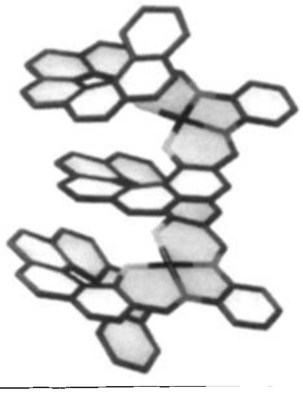
1a, 1b **2**

M. Schmittel,* R. Söllner 2107–2109

First Characterization of a Titanium Enolate Radical Cation in Solution: Carbon–Carbon Bond Formation and the Kinetics of the Mesolytic Ti–O Bond Cleavage

---

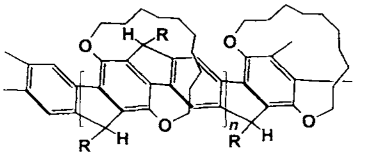
Coordinating the Schiff base of a helicenecdicarbaldehyde to nickel centers resulted in the first ladder polymer that has an unbroken network of double bonds winding in one direction along a helix (see the representation on the right). Helicene and nickel salophen units alternate in the product, on average 8.3 times.



Y. Dai, T. J. Katz,*
D. A. Nichols 2109–2111

Synthesis of a Helical Conjugated Ladder Polymer

A chiroptically active compound without a helical structure has been constructed in the ladder polymer **1** (R = 3,4-$C_6H_3(OC_6H_{13})_2$), which has been synthesized from the corresponding enantiomerically pure $OC_{10}H_{20}O$-bridged diboronic acid. The molar ellipticity of **1** [2.2×10^6 rad cm^2 mol^{-1} (461 nm)] leads to an anisotropy factor of $g = 0.003$, which is thus only an order of magnitude less than the maximum value (0.02) for chiral conjugated polymers so far reported.



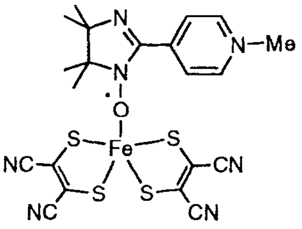
1

R. Fiesel, J. Huber,
U. Scherf* 2111–2113

Synthesis of an Optically Active Poly(*para*-phenylene) Ladder Polymer

---

A novel combination of $S = 1/2$ and $S = 3/2$ spin crossover and magnetic interaction between ligand and central metal exists in the iron(III) complex **1**. Compound **1** is readily accessible from the corresponding dimeric thiolatoferrate(III) complex and the corresponding pyridinium salt, and offers a further example for the diversity of properties of molecular magnetic materials.



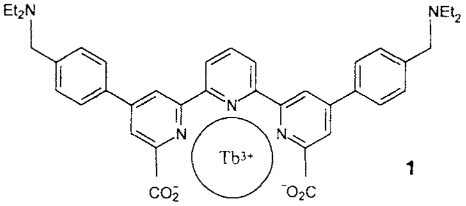
1

J.-P. Sutter, M. Fettouhi, L. Li,
C. Michaut, L. Ouahab,*
O. Kahn* 2113–2116

Synergy between Magnetic Interaction and Spin Crossover in an Iron(III) Complex with an Organic Radical as Ligand

---

The green luminescence of the terbium complex **1** is increased by a factor of 16 when the amino groups in the side chains are protonated. Because its luminescence has a lifetime of 0.62 ms, this complex can serve as an effective pH sensor in intrinsically fluorescent environments.



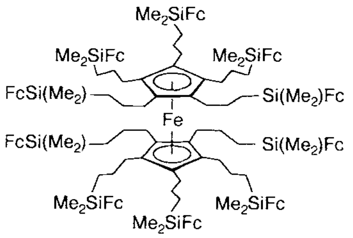
1

A. P. de Silva,* H. Q. N. Gunaratne,
T. E. Rice 2116–2118

Proton-Controlled Switching of Luminescence in Lanthanide Complexes in Aqueous Solution: pH Sensors Based on Long-Lived Emission

---

The decaferrocenyl ferrocene 1, prepared readily from decaallylferrocene by hydrosilylation, is an ideal substrate for further ($n \times 10$)-fold functionalization. Highly functionalized compounds such as **1** are of interest as building blocks for redox-active polymers and as molecular electron reservoirs. Fc = ferrocenyl.



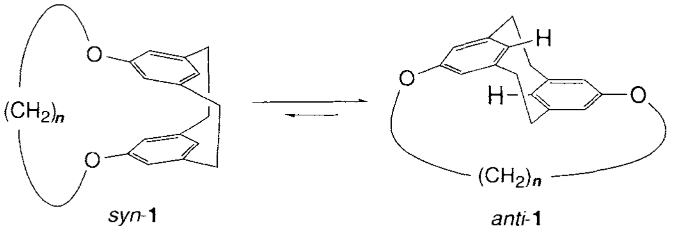
1

P. Jutzi,* C. Batz, B. Neumann,
H.-G. Stammler 2118–2121

Maximum Functionalization of Metallocenes: Decaallylferrocene and Derivatives

---

The tether length determines the conformation of [2.2]metacyclophane **1**. The cyclophane with the 13-atom tether ($n = 11$) exists at room temperature as an equilibrium mixture of *syn* and *anti* isomers (ca. 5.9:1), whereas the next lower homologue ($n = 10$) in this series adopts only the *syn* conformation and the next higher homologue ($n = 12$) solely the *anti* conformation.



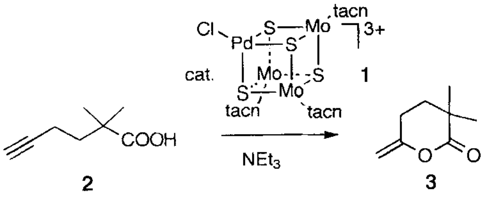
syn-**1**   *anti*-**1**

G. J. Bodwell,* T. J. Houghton,
J. W. J. Kennedy,
M. R. Mannion* 2121–2123

First-Generation Tethered [2.2]Metacyclophanes-Prototypes of Molecular Devices

0570-0833 96 3518-2010 $ 15.00 + .25 0

Catalytic activity remarkably higher than that of mononuclear palladium catalysts is exhibited by the cuboidal sulfide cluster **1** (tacn = 1,4,7-triazacyclononane) in the lactonization of alkynoic acids (**2** → **3**). The reaction can even be conducted in water owing to the good solubility and stability of the cluster in this medium.

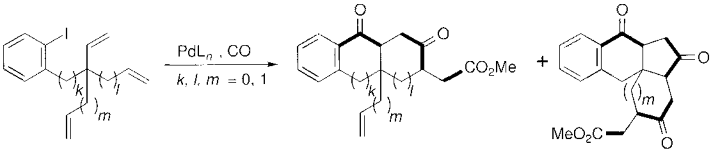


T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai* 2123–2124

A Novel Catalyst with a Cuboidal $PdMo_3S_4$ Core for the Cyclization of Alkynoic Acids to Enol Lactones

---

Up to seven C–C bonds are formed in an acylpalladation cyclization cascade that relies on the use of carbon monoxide as a one-carbon unit [Eq. (a)]. This reaction not only provides an efficient synthesis of polycycles but is also the first example of a carbometalation cascade giving products with an angular mode of ring fusion.

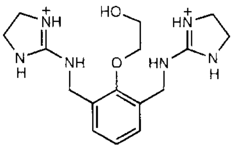


C. Copéret, S. Ma, E. Negishi* 2125–2126

Palladium-Catalyzed Carbonylative Cyclization Cascades with Iododienes and -trienes

---

A million times faster! The phosphorylation of **1**, in which the heterocyclic cations mimic the arginine residues at positions 35 and 87 in staphylococcal nuclease, is significantly faster than the analogous reaction of uncharged alcohols. Compound **1** is the most reactive mimetic of this enzyme.



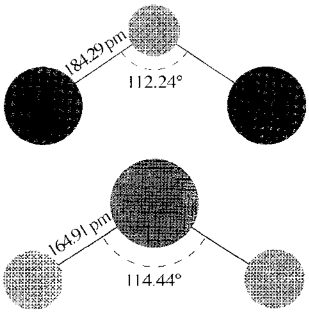
1

M.-S. Muche, M. W. Göbel* 2126–2129

Bis(guanidinium) Alcohols as Models of Staphylococcal Nuclease: Substrate Binding through Ion Pair Complexes and Fast Phosphoryl Transfer Reactions

---

Two bromine oxides with more than two atoms have been structurally characterized for the first time in the gas phase (see picture on the right; top: Br_2O, bottom: OBrO). Both molecules occur over a solid product formed in the reaction of O and Br_2. Under certain conditions BrO, OBrO, and Br_2O were obtained simultaneously.

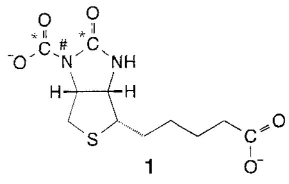


H. S. P. Müller,* C. E. Miller, E. A. Cohen 2129–2131

Dibromine Monoxide, Br_2O, and Bromine Dioxide, OBrO: Spectroscopic Properties, Molecular Structures, and Harmonic Force Fields

---

The enzymatic carboxylation of carboxybiotin (**1**) at the N-1′ nitrogen atom was proved unequivocally by the observation of ^1J(C,N) and ^2J(C,C) spin–spin coupling constants in NMR experiments. Essential to these studies was the use of the labeled substrates [1′-^{15}N]- and [2′-^{13}C]biotin along with [1,5-$^{13}C_2$]-glutaconate as the source of $^{13}CO_2$.

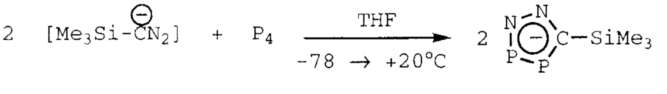


S. Berger,* A. Braune, W. Buckel,* U. Hertel, M.-L. Lee 2132–2133

Enzyme-Catalyzed Formation of Carboxybiotin as Proved by the Measurement of ^{15}N,^{13}C and ^{13}C,^{13}C Spin–Spin Coupling

---

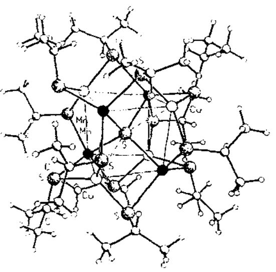
A formal [2+3]cycloaddition between |P≡P| and a diazomethyl anion affords the anionic, aromatic five-membered ring $[RCP_2N_2]^-$ (R = Me_3Si) [Eq. (a); counterion Li^+]. This reaction is a rare example of the use of P_4 in organic synthesis.



C. Charrier, N. Maigrot, L. Ricard, P. Le Floch, F. Mathey* 2133–2134

The Reaction of White Phosphorus with Lithium (Trimethylsilyl)diazomethanide: Direct Access to a New, Aromatic 1,2,3,4-Diazadiphosphole Ring

The cubane-like Mn_4Cu_4 framework with an interstitial μ_4-S ion is the outstanding feature of **1**, the octanuclear mixed-metal complex that is formed by the reaction of $(Me_4N)_2[Mn_2(S\mathit{i}C_3H_7)_6]$ with CuCl in acetonitrile. The Mn_4S_{13} core of **1** can be considered as a minimal fragment of the sphalerite-type structure.



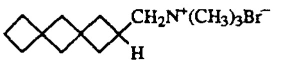
1

H.-O. Stephan, M. G. Kanatzidis, G. Henkel* 2135–2137

$[Cu_4Mn_4(S\mathit{i}C_3H_7)_{12}S]^{2-}$, a Novel Octanuclear Heterometallic Complex Consisting of a Metal Cube with an Interstitial μ_4-Sulfide Ion and Edge-Bridging Thiolate Ligands

---

Micelles are usually highly disorganized. But how do surfactants with rigid linear hydrophobic chains behave? The linear spiro-surfactants **1** and **2**, which were prepared in multistep syntheses, display very different relationships between surface tension and surfactant concentration. Spiro-phospholipids were also prepared and found to have exceptionally high transition temperatures.



1

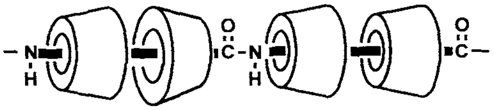
2

F. M. Menger,* J. Ding 2137–2139

Spiro-Surfactants and -Phospholipids: Synthesis and Properties

---

Molecular nylon threads that are completely encased by cyclodextrin molecules (see sketch below) can be synthesized by solid-state polycondensation of α,ω-amino acids in channellike cyclodextrin inclusion compounds. Since the polyamide chains are covered with cyclodextrins, they are soluble in water, but only for a limited time, because the rings tend to slowly unthread to some extent.

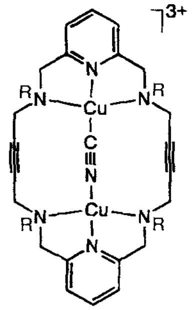


M. B. Steinbrunn, G. Wenz* 2139–2141

Synthesis of Water-Soluble Inclusion Compounds from Polyamides and Cyclodextrins by Solid-State Polycondensation

---

A highly selective response of a microelectrode to cyanide ions is induced by the lipophilic dicopper(II) macrocyclic complex $[(L)Cu_2(NO_3)_4]$ (L = polyazamacrocycle; see structural formula on the right) embedded in a PVC liquid membrane. The complex is the first example of a new type of anion-selective ionophore. The target anion is efficiently incorporated by a molecular recognition process. R = $C_{16}H_{33}$.

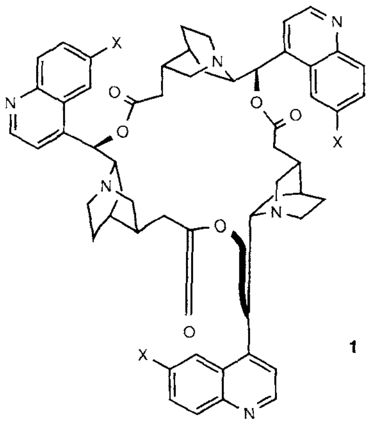


B. Ahlers, K. Cammann,* S. Warzeska, R. Krämer* 2141–2143

Molecular Recognition of Cyanide by a Dicopper(II) Macrocyclic Ionophore: Construction of a Cyanide-Selective Liquid-Membrane Electrode

---

A remarkably narrow product distribution is observed in the thermodynamic cyclization of modified Cinchona alkaloids to yield predominantly the trimer **1** (X = H, OMe); this is a representative of a new class of macrocycle. The reaction was proved to be reversible by resubmitting the cinchonidine (X = H) and quinine (X = OMe) to the reaction conditions: a statistical mixture of all four possible trimers was obtained.

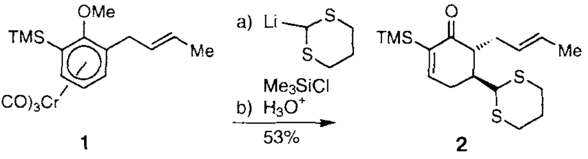


1

S. J. Rowan, P. A. Brady, J. K. M. Sanders* 2143–2145

Structure-Directed Synthesis under Thermodynamic Control: Macrocyclic Trimers from Cinchona Alkaloids

Chlorotrimethylsilane is the reagent of choice to trap the ionic intermediate that arises on nucleophilic addition to *ortho*-substituted anisoletricarbonylchromium complexes and to suppress its tendency toward *tele*-substitution (relative to the methoxy group). Thus the planar-chiral complex **1** can be transformed into the cyclohexenone **2** with complete retention of the stereochemical information in greater than 95% *ee*. Compound **2** is a promising precursor for the total synthesis of (+)-ptilocaulin.



H.-G. Schmalz,*
K. Schellhaas 2146–2148

Controlling the Course of Nucleophilic Additions to *ortho*-Substituted (η^6-Anisole)-tricarbonylchromium Complexes: Dienol Ether Formation versus *tele*-Substitution

Complex libraries composed of more than five thousand cyclopeptides can act as chiral selectors when added to the mobile phase in capillary electrophoresis. Cyclohexapeptide sublibraries (such as those listed below) were used to achieve baseline separations of enantiomers of N^α-dinitrophenyl (DNP) and 9-fluorenylmethoxycarbonyl (FMOC) amino acids and Tröger's base. This approach can be used to identify selectors for difficult-to-separate racemates.

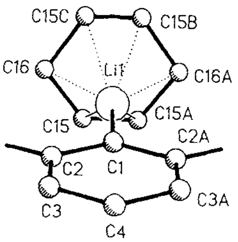
c[DFXXXa] c[RKXXXa] c[OOXXXO]

G. Jung,* H. Hofstetter, S. Feiertag,
D. Stoll, O. Hofstetter,
K.-H. Wiesmüller,
V. Schurig* 2148–2150

Cyclopeptide Libraries as New Chiral Selectors in Capillary Electrophoresis

Stabilized only by steric effects and weak solvation by benzene, the aryllithium compound **1** exists as a monomeric benzene adduct. The unique structure of **1** in the solid state is shown on the right; the *ortho* substituents on the η^1-bound phenyl ring have been omitted for clarity.

$C_6H_6 \cdot LiC_6H_3$-2,6-(2,4,6-iPr$_3C_6H_2)_2$ **1**



B. Schiemenz, P. P. Power* ... 2150–2152

Synthesis and Structure of a Unique Monomeric σ-Bonded Aryllithium Compound Stabilized by a Weak Li–Benzene π Interaction

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* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the second September issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2157.

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