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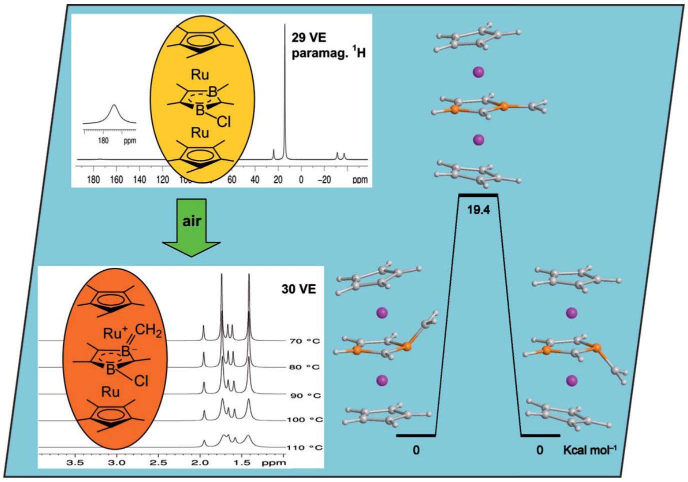
COVER PICTURE

The cover picture shows the serendipitous transformation of the yellow into the dark orange triple-decker sandwich complex by air. The unique $B{=}CH_2$ group formed strongly leans toward one of the metal atoms. Non-equivalence of the Cp*Ru groups suggests a bridge inversion, which does not occur below 70 °C. At higher temperatures the signals of the Cp* protons broaden, but coalescence is not reached in toluene. Details are discussed in the article by M. Enders, A. R. Kudinov, W. Siebert et al. on p. 2911ff.



CONTENTS

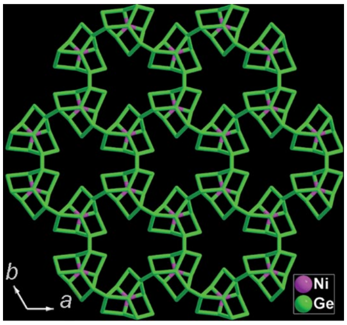
MICROREVIEW

Germanate Frameworks

Z.-E. Lin, G.-Y. Yang* **2895–2902**

Germanate Frameworks Constructed from Oxo Germanium Cluster Building Units

Keywords: Microporous materials / Open frameworks / Germanium / Cluster compounds / Structure elucidation



Open-framework germanate structures can be achieved by the organization of oxo germanium clusters into extended frameworks with a variety of topologies.

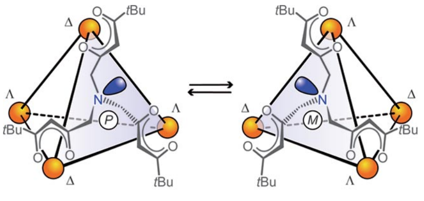
SHORT COMMUNICATIONS

VT NMR

R. W. Saalfrank,* H. Maid, A. Scheurer, R. Puchta, W. Bauer **2903–2906**

Mesomerization of S_4-Symmetric Tetrahedral Chelate Complex $[In_4(L^3)_4]$: First-Time Monitored by Temperature-Dependent ^1H NMR Spectroscopy

Keywords: Bailar twist / NMR spectroscopy / Density functional calculations / Indium / N,O ligands / Supramolecular chemistry



$(\Delta,\Delta,\Lambda,\Lambda)(P,P,M,M)\text{-}[In_4(L^3)_4]\text{-}\mathbf{3} \rightleftarrows (\Lambda,\Lambda,\Delta,\Delta)(M,M,P,P)\text{-}[In_4(L^3)_4]\text{-}\mathbf{3'}$

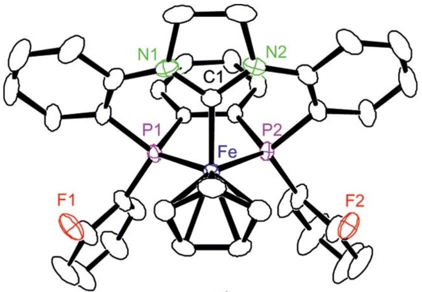
Exposing a poker face: Symmetry breaking of the C_3-tripodal tris(bidentate) chelators $(L^3)^{3-}$ during complexation with In^{3+} ions afforded S_4-symmetric $[In_4(L^3)_4]$ (**3**). The manifold stereochemical features of this unique structure and its non-dissociative mesomerization process (**3** ⇄ **3′**) was exposed by VT ^1H NMR spectroscopy.

NHC–Diphosphane Macrocycles

A. Flores-Figueroa, T. Pape, J. J. Weigand, F. E. Hahn* **2907–2910**

Template-Controlled Formation of an [11]-ane-P_2C^{NHC} Macrocyclic Ligand at an Iron(II) Template

Keywords: Macrocyclic ligands / Carbenes / Phosphanes / Iron

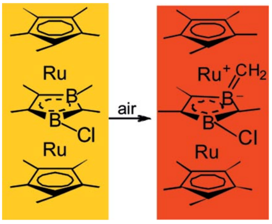


[1]$^+$

The [11]ane-P_2C^{NHC} macrocycle in cation $[\mathbf{1}]^+$ has been generated in a template-controlled reaction at iron(II). The macrocycle was synthesized in high overall yield by a base-induced elimination of 2 equiv. of HF from the *facially* coordinated complex with an NH,NH-stabilized NHC ligand and a diphosphane bearing fluoro-substituted phenyl substituents.

Triple-Decker Complexes

Refluxing of a mixture of $[Cp^*RuCl]_4$ and pentamethyl-2,3-dihydro-1,3-diborole in thf leads to the paramagnetic triple-decker complex. Exposed to air it slowly looses a hydrogen atom in CH_2Cl_2 to give the diamagnetic triple-decker complex with a bridging dihydro-diborafulvene derivative whose unique $B{=}CH_2$ group is strongly bent toward one of the ruthenium atoms.



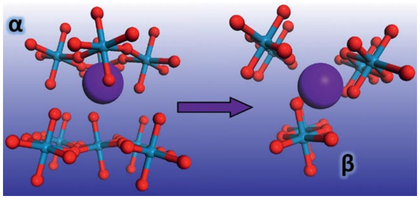
E. V. Mutseneck, H. Wadepohl, M. Enders,* A. R. Kudinov,* W. Siebert* ... 2911–2918

Paramagnetic (1,3-Diborolyl)ruthenium Triple-Decker Complexes and Transformation into Diamagnetic Complexes Having Bridging 1,3-Diborafulvene Ligands

Keywords: Ruthenium / Sandwich compounds / Dihydrodiborafulvene / Paramagnetic triple-decker / Slipped triple-decker

A Polymorphic Fluoroargentate

The 2D layered structure of α-K_2AgF_4 easily collapses to a 1D chain structure of β-K_2AgF_4 due to the insufficient size of the K^+ cation.

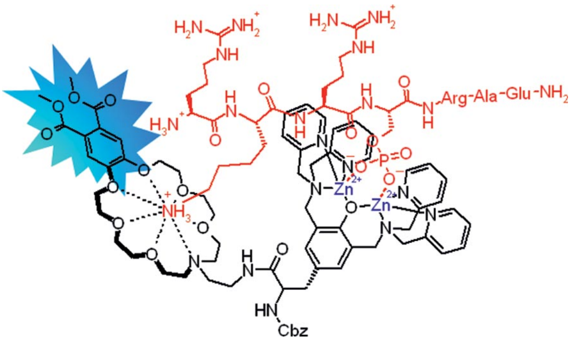


D. Kurzydłowski,* M. Derzsi, A. Budzianowski, Z. Jagličić, W. Koźmiński, Z. Mazej, W. Grochala 2919–2925

Polymorphism of Fluoroargentates(II): Facile Collapse of a Layered Network of α-K_2AgF_4 Due to the Insufficient Size of the Potassium Cation

Keywords: Silver / Fluorides / Polymorphism / Potassium

Peptide Recognition



Phosphorylated peptides are selectively bound in water by synthetic receptors consisting of a metal complex and a luminescent crown ether. Reversible coordination of the phosphate ion to the metal complex allows the intramolecular interaction of the ammonium ion and the crown ether, which triggers an increase in emission.

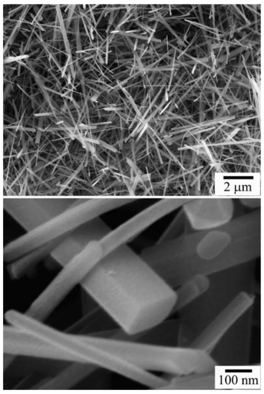
A. Späth, C. Koch, B. König* 2926–2935

Luminescent Hybrids Combining a Metal Complex and a Crown Ether – Receptors for Peptidic Ammonium Phosphates

Keywords: Crown compounds / Zinc / N ligands / Peptides / Luminescence / Amines / Cations

Hexatitanate Whiskers

Well-developed, highly crystalline $Na_2Ti_6O_{13}$ photocatalyst whiskers were grown by cooling a NaCl flux at a relatively low temperature of 700 °C. The 1D $Na_2Ti_6O_{13}$ whiskers demonstrated good photocatalytic activity under UV light irradiation. The effects of the holding temperature, solute concentration, and cooling rate on the downsizing of the $Na_2Ti_6O_{13}$ whiskers were studied.



K. Teshima,* S. H. Lee, S. Murakoshi, S. Suzuki, K. Yubuta, T. Shishido, M. Endo, S. Oishi 2936–2940

Highly Crystalline, Idiomorphic $Na_2Ti_6O_{13}$ Whiskers Grown from a NaCl Flux at a Relatively Low Temperature

Keywords: Crystal growth / Photochemistry / Titanates / Photocatalysis

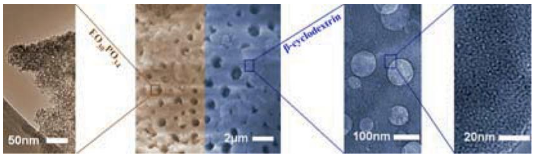
CONTENTS

Hierarchical Porous Phosphonates

T.-Y. Ma, Z.-Y. Yuan* 2941–2948

Organic-Additive-Assisted Synthesis of Hierarchically Meso-/Macroporous Titanium Phosphonates

Keywords: Organic-inorganic hybrid composites / Titanium / Phosphonates / Adsorption / Mesoporous materials



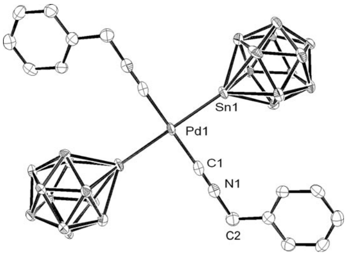
Hierarchically meso-/macroporous titanium triphosphonate hybrid materials have been prepared with the assistance of the diblock copolymer $EO_{30}PO_{34}$ and β-cyclodextrin. The synthesized materials have been proved to be efficient adsorbents for heavy metal ions and CO_2.

Palladium Isocyanide Chemistry

M. Hornung,
L. Wesemann* 2949–2955

Palladium Chemistry with Stanna-*closo*-dodecaborate and Isocyanides

Keywords: Palladium / Tin / Boron / Cluster compounds / Insertion / Isocyanide



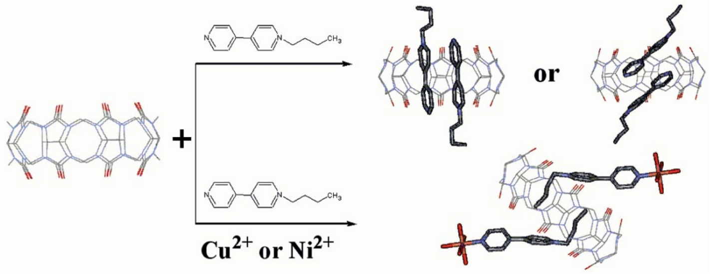
Palladium coordination chemistry with isocyanides and the tin ligand stanna-*closo*-doedcaborate is presented. Insertion reactions result in the formation of zwitterionic molecules.

Host–Guest Chemistry

X. Xiao, J.-X. Liu, K. Chen, Q.-J. Zhu,
S.-F. Xue, Z. Tao* 2956–2961

Metal Cation Controlled Supramolecular Assembly of 1-Butyl-4,4′-bipyridinium and Cucurbit[8]uril

Keywords: Host-guest systems / Self-assembly / Molecular recognition / Supramolecular chemistry



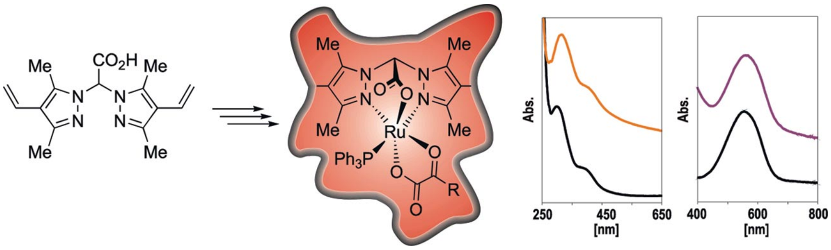
Three supramolecular assemblies consisting of cucurbit[8]uril (Q[8]) and 1-butyl-4,4′-bipyridinium were synthesized in aqueous solution. Q[8] can interact with the bipyridinium to form highly stable 1:2 ternary complexes, and it can selectively encapsulate the bipyridinium or butyl moiety of the guest in its hydrophobic cavity to form ternary complexes through control of the metal–ligand coordination.

Ligand Design

G. Türkoglu, C. Pubill Ulldemolins,
R. Müller, E. Hübner, F. W. Heinemann,
M. Wolf, N. Burzlaff* 2962–2974

Bis(3,5-dimethyl-4-vinylpyrazol-1-yl)acetic Acid: A New Heteroscorpionate Building Block for Copolymers that Mimic the 2-His-1-carboxylate Facial Triad

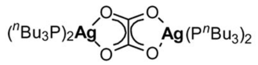
Keywords: Ligand design / Copolymerisation / Manganese / Rhenium / Ruthenium / Tripodal ligands

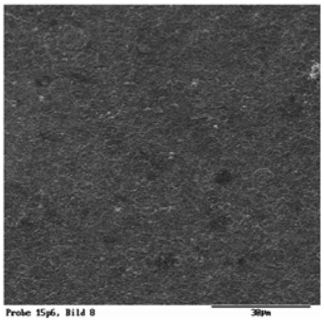


The new scorpionate ligand bis(3,5-dimethyl-4-vinylpyrazol-1-yl)acetic acid (Hbdmvpza) is suitable for copolymerisation with MMA or EGDMA. Immobilised manganese, rhenium, iron and copper complexes as well as embedded ruthenium "dummy" complexes that mimic the active site of 2-oxoglutarate dependent iron oxygenases have been investigated.

Ag Complexes for Deposition

Straightforward synthesis methodologies for the preparation of several phosphane disilver dicarboxylate and squarate complexes are presented. The application of selected disilver compounds in CVD and spin-coating processes for the deposition of silver films is discussed.





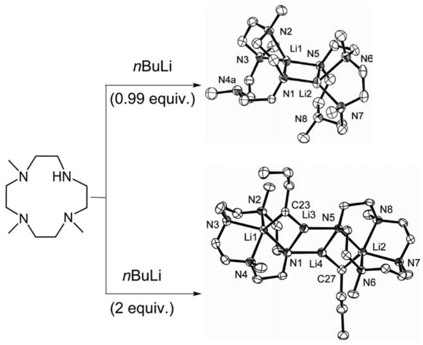
A. Jakob, T. Rüffer, H. Schmidt, P. Djiele, K. Körbitz, P. Ecorchard, T. Haase, K. Kohse-Höinghaus, S. Frühauf, T. Wächtler, S. Schulz, T. Gessner, H. Lang* 2975–2986

Disilver(I) Coordination Complexes: Synthesis, Reaction Chemistry, and Their Potential Use in CVD and Spin-Coating Processes for Silver Deposition

Keywords: Silver / Phosphanes / Dicarboxylate ligands / Thin films / Chemical vapor deposition

Metalation of Cyclen

The cyclic polyamine (Me$_3$TACD)H was treated with *n*BuLi to yield a lithiated product that is dimeric in the solid state. When an excess of *n*BuLi is utilized, tri- and tetranuclear aggregates are formed. These compounds have been characterized in the solid state by single-crystal X-ray diffraction and in solution by NMR spectroscopy.



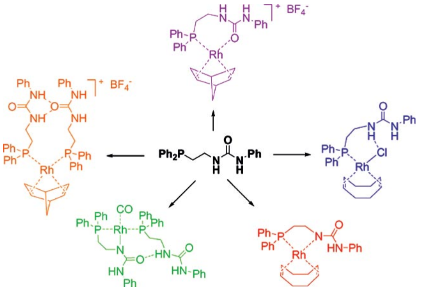
S. Standfuss, T. P. Spaniol, J. Okuda* 2987–2991

Lithiation of a Cyclen-Derived (NNNN) Macrocycle and Its Reaction with *n*-Butyllithium

Keywords: Cyclens / Amides / Metalation / Lithium / Ladder structures

Ligand Design

We present ureaphosphane ligands that, depending on the nature of the anion and the metal/ligand ratio, coordinate as either hybrid, anionic or supramolecular bidentate ligands to rhodium. The different complexes were investigated in the asymmetric hydrogenation reaction.

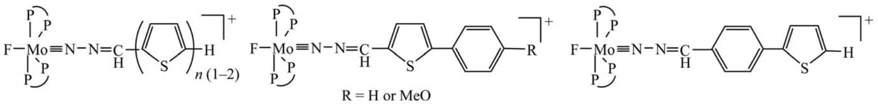


J. Meeuwissen, R. Detz, A. J. Sandee, B. de Bruin, M. A. Siegler, A. L. Spek, J. N. H. Reek* 2992–2997

Ureaphosphanes as Hybrid, Anionic or Supramolecular Bidentate Ligands for Asymmetric Hydrogenation Reactions

Keywords: Asymmetric hydrogenation / Rhodium / Phosphorus ligands / Coordination chemistry / Hydrogen bonds

NLO Organometallic Materials



New molybdenum complexes *trans*-[FMo(N=NCHL)(dppe)$_2$][BF$_4$] {L = (bi)thienyl or arylthienyl} were prepared and fully characterized. The study of the electrochemical, spectroscopic and optical (linear and nonlinear) properties showed that the new molybdenum complexes could be strong candidates for the applications that exploit materials with good nonlinear properties.

A. M. Fonseca*, M. Belsley, E. M. Gomes, M. C. R. Castro, M. M. M. Raposo 2998–3004

Molybdenum Complexes Bearing (Bi)thienyl- or Arylthienyl-Substituted π-Conjugated Spacers: Synthesis, Electrochemical, Spectroscopic and Nonlinear Optical Properties

Keywords: Molybdenum / Electrochemistry / Solvatochromism / Nonlinear optics / Thiophene

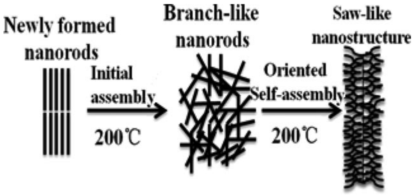
CONTENTS

Nanostructured Metal Tellurides

L. Jiang, Y.-J. Zhu,*
J.-B. Cui **3005–3011**

Nanostructures of Metal Tellurides (PbTe, CdTe, $CoTe_2$, Bi_2Te_3, and Cu_7Te_4) with Various Morphologies: A General Solvothermal Synthesis and Optical Properties

Keywords: Tellurium / Nanostructures / Self-assembly / Luminescence / Reaction mechanisms



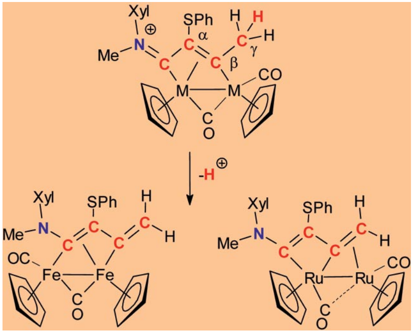
A general surfactant-assisted solvothermal route was developed for the synthesis of a variety of metal telluride nanostructures with varied morphologies in mixed solvents of ethylene glycol and water. The optical properties of the as-prepared nanostructures were investigated.

γ-Deprotonation

L. Busetto, F. Marchetti, M. Salmi,
S. Zacchini, V. Zanotti* **3012–3021**

γ-Deprotonation of Bridging Vinyliminium Ligands: New Route to Aminobutadienylidene Diiron and Diruthenium Complexes

Keywords: Vinylidene ligands / Deprotonation / Iron / Ruthenium / Dinuclear complexes



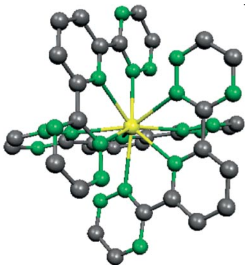
Conjugated iminium ions (as bridging vinyliminium ligands) can undergo γ-deprotonation to form dienamines, which are stabilized by dinuclear coordination. Two different coordination modes have been evidenced.

Selective Metal Ion Extraction

S. Trumm,* P. J. Panak, A. Geist,
T. Fanghänel **3022–3028**

A TRLFS Study on the Complexation of Cm^{III} and Eu^{III} with 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in Water/Methanol Mixture

Keywords: Actinides / Lanthanides / Fluorescence spectroscopy / Thermodynamics / Partitioning



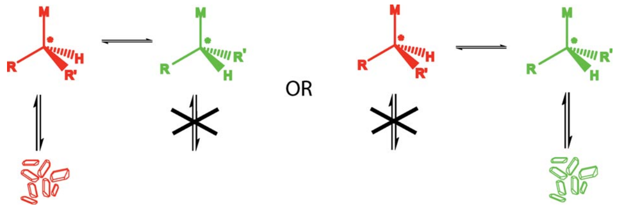
Stability constants of $[M(n\text{Pr-BTP})_3]^{3+}$ complexes of Cm^{III} and Eu^{III} in water/methanol, 1:1 are determined using time-resolved laser fluorescence spectroscopy. Enthalpy of complexation is identified as the molecular driving force of BTPs' ability to selectively extract Cm^{III} and Am^{III} in the presence of trivalent lanthanides as required in the SANEX process.

Absolute Asymmetric Synthesis

A. Lennartson*, J. Sundberg, T. Wiklund,
G. Hilmersson,
M. Håkansson* **3029–3039**

Spontaneous Resolution and Carbonation of Chiral Benzyllithium Complexes

Keywords: Chiral resolution / Enantioselectivity / Lithium compounds / Crystal engineering / Asymmetric synthesis



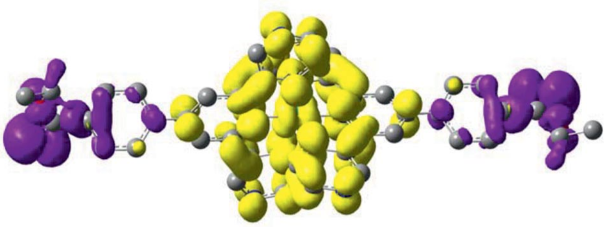
Stereochemically labile organometallic reagents that crystallise as conglomerates may undergo total spontaneous resolution. We set out to isolate an α-substituted benzyllithium complex crystallising as such a conglomerate, in order to be able to trap the chirality of the labile reagent by reaction with carbon dioxide.

Ligand Effects

A. Stublla, P. G. Potvin* 3040–3050

Ruthenium(II) Complexes of Carboxylated Terpyridines and Dipyrazinylpyridines 💻

Keywords: Ruthenium / Ligand effects / Density functional calculations / Carboxylation / Electronic structure



This study reports the synthesis, molecular structure, electronic structure, spectroscopy and electrochemistry of complexes of singly carboxylated tridentate ligands, with and without phenylene spacers, in free acid and ester forms. Phenylene spacers acted as electron-donating groups tempering the effects of carboxyl groups, and the lowest-energy transitions had strong intraligand character.

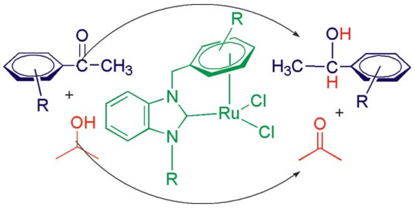
Transfer Hydrogenation

N. Gürbüz, S. Yaşar, E. Ö. Özcan, İ. Özdemir,* B. Çetinkaya 3051–3056

Transfer Hydrogenation of Ketones by Ruthenium Complexes Bearing Benzimidazol-2-ylidene Ligands

Keywords: Nitrogen heterocycles / Carbene ligands / Ruthenium / Hydrogenation / Ketones

Novel benzimidazol-2-ylidene ruthenium(II) complexes were prepared and characterized. These complexes are efficient catalysts for the transfer hydrogenation of different ketones.



CORRECTION

Keywords: Hemiporphyrazines / Phthalocyanines / Silver / Carbahemiporphyrazines / Agostic interactions

Dihydroxy- and Tetrahydroxydicarbahemiporphyrazine: Phthalocyanine Analogues with Phenol and Resorcinol Units

N. Barone, R. Costa, S. Sripothongnak, C. J. Ziegler* 3057

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* Author to whom correspondence should be addressed.

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