

Contents

Special Issue: 11th International Symposium on Inorganic Ring Systems

Preface 2607

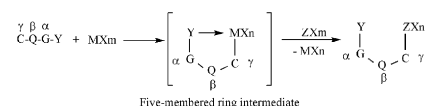
Review

Iwao Omae

J. Organomet. Chem. 692 (2007) 2608

Three types of reactions with intramolecular five-membered ring compounds in organic synthesis

There are three types of reactions with intramolecular five-membered ring compounds in organic syntheses: The first type is reactions involving intramolecular five-membered ring compounds. The second is reactions performed via the intermediates. The third is the metal-catalyzed reactions.



MX_m, MX_n = metal compounds
M = transition metals and main group metals,
65 kinds of metals
Y = N, P, O, S, etc.
G, Q = C, N, P, O, S, etc.
ZX_m, ZX_n = substrates

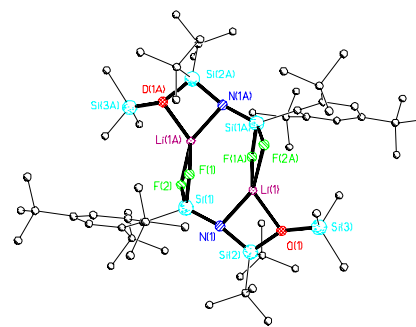
Mini-reviews

Uwe Klingebiel, Christoph Matthes

J. Organomet. Chem. 692 (2007) 2633

From lithiumhalosilylamide to small and large ring compounds, iminosilenes and iminosilanes

The structural make-up of lithium-halosilylamides depends very much on the solvent used. These lithium salts are useful building blocks for the synthesis of e.g. Si-N-rings, iminosilanes and iminosilenes.



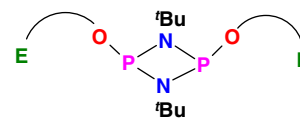
Crystal structure of (Me₃C)₂Si(OSiMe₃)NLiF₂Si-2,4,6-C₆H₂(CMe₃)₃

Maravanji S. Balakrishna, P. Chandrasekaran, Ramalingam Venkateswaran

J. Organomet. Chem. 692 (2007) 2642

Functionalized cyclodiphosphazanes *cis*-[^tBuNP(OR)]₂ (R=C₆H₄OMe-*o*, CH₂CH₂OMe, CH₂CH₂SMe, CH₂CH₂NMe₂) as neutral 2e, 4e or 8e donor ligands

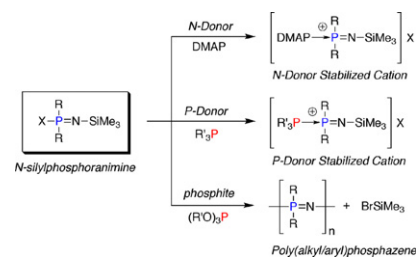
Cyclodiphosphazanes containing donor functionalities on phosphorus(III) centers can act as 2e, 4e, 6e or 8e donors depending on the nature of the metal derivatives employed, stoichiometry and the reaction conditions.



Keith Huynh, Ian Manners*J. Organomet. Chem.* 692 (2007) 2649

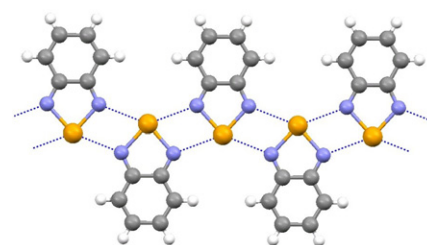
Isolation of donor-stabilized *N*-silylphosphoranimine cations and the discovery of an ambient temperature route to Poly(alkyl/aryl)phosphazenes

The *N*-silylphosphoranimine $\text{Cl}_3\text{P}=\text{NSiMe}_3$ reacts with strong pyridine and phosphine bases to yield *N*-donor-stabilized cations and *N*-phosphinophosphoranimines, respectively. The later reaction occurs via a phosphine mediated dehalogenation mechanism. Reactions involving phosphines and phosphites with the phosphoranimine $\text{BrR}_2\text{P}=\text{NSiMe}_3$, respectively, yields *P*-donor stabilized cations and poly(alkyl/aryl)phosphazenes at ambient temperature.

**Anthony F. Cozzolino, Ignacio Vargas-Baca***J. Organomet. Chem.* 692 (2007) 2654

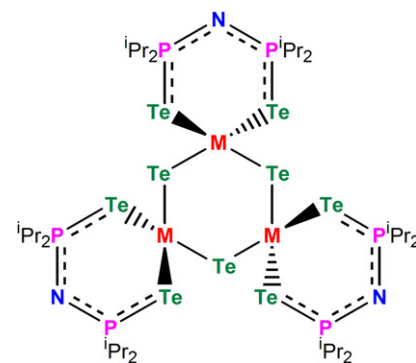
The supramolecular chemistry of 1,2,5-chalcogenadiazoles

1,2,5-Chalcogenadiazoles, in particular the tellurium derivatives, are promising building blocks for the assembly supramolecular structures through the formation of the $[\text{E}-\text{N}]_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) supramolecular synthon.

**Tristram Chivers, Jari Konu, Jamie S. Ritch, May C. Copley, Dana J. Eisler, Heikki M. Tuononen***J. Organomet. Chem.* 692 (2007) 2658

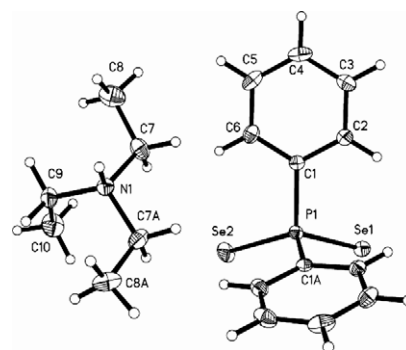
New tellurium-containing ring systems

This personal account provides an overview of the chemistry of the ditelluroimidodiphosphinate ligands $[\text{TePR}_2\text{NPR}_2\text{Te}]^-$ ($\text{R} = \text{Ph}, \text{'Pr}, \text{'Bu}$) with an emphasis on the formation of new tellurium-containing ring systems in: (a) redox processes and (b) the formation of metal complexes.

**Regular Papers****Chinh Q. Nguyen, Mohammad Afzaal, Mohammad A. Malik, Madeleine Helliwell, Jim Raftery, Paul O'Brien***J. Organomet. Chem.* 692 (2007) 2669

Novel inorganic rings and materials deposition

The synthesis of imino-dialkylphosphinate ligands $[(\text{EPR}_2)_2\text{NH}]$ ($\text{E} = \text{Se}$ or Te) and dialkyldiselenophosphinate ligands $(\text{HNEt}_3)(\text{R}_2\text{PSe}_2)$ is discussed along with their usefulness as either thin films or nanoparticles.

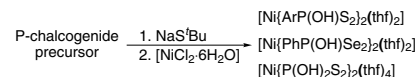


Weifeng Shi, Rebecca Kelting,
Maryam Shafaei-Fallah,
Alexander Rothenberger

J. Organomet. Chem. 692 (2007) 2678

Transformations of P-chalcogenide precursors with a hydrated metal salt

Nucleophilic fragmentation reactions of neutral P-chalcogenides with alkali metal salts and subsequent metatheses with hydrated transition metal salts are illustrated by a case study which produced $[\text{Ni}\{\text{ArP}(\text{OH})\text{S}_2\}_2(\text{thf})_2]$ (**1**) (Ar = 4-anisyl), $[\text{Ni}\{\text{PhP}(\text{OH})\text{Se}_2\}_2(\text{thf})_2]$ (**2**) and $[\text{Ni}\{\text{P}(\text{OH})_2\text{S}_2\}_2(\text{thf})_4]$ (**3**).

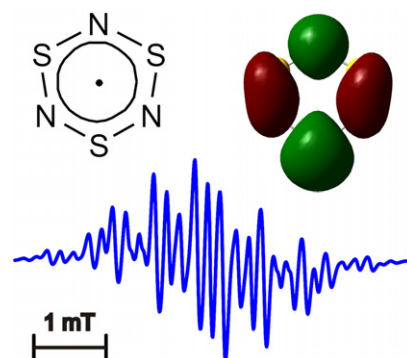


René T. Boéré, Heikki M. Tuononen,
Tristram Chivers, Tracey L. Roemmele

J. Organomet. Chem. 692 (2007) 2683

Structures and EPR spectra of binary sulfur–nitrogen radicals from DFT calculations

DFT calculations are proving to be of immense value in the rapid calculation of hyperfine coupling (hfc) constants of main group element free radicals. Predictions can be made not only for the commonly observed isotopes, but also for those that are experimentally hard to observe for reasons of low abundance or spins >1, such as ^{33}S . Using calculated hfc constants, we predict that the never-observed isotropic EPR spectrum of $[\text{S}_3\text{N}_3]$ would be more diagnostic if obtained on a sample with modest (30%) enrichment in ^{33}S content than if obtained at natural abundance, as shown in a simulation employing realistic line-widths.

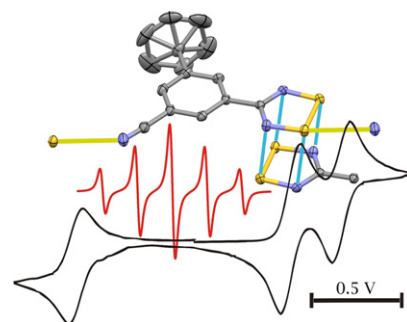


René T. Boéré, Lai-Yoong Goh,
Chwee Ying Ang, Seah Ling Kuan,
Hiu Fung Lau, Victor Wee Lin Ng,
Tracey L. Roemmele, Sonja D. Seagrave

J. Organomet. Chem. 692 (2007) 2697

A *tert*-butyl/cyano substituted (1,2,3,5-dithiadiazolyl)benzene and η^2 π complexes with $\text{CpCr}(\text{CO})_2$

Main group ring compounds are a rich and diverse source of thermodynamically stable free radicals, yet the ability of such radicals to act as ligands in coordination chemistry has received only limited attention. We recently reported an unprecedented η^2 coordinated π complex of 5-*tert*-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene with $\text{CpCr}(\text{CO})_2$. The synthesis, crystal structure, EPR spectrum and cyclic voltammetry of the main group free radical is described here in detail, and the intermolecular contacts observed in its crystal structure are contrasted to those found in the complex.

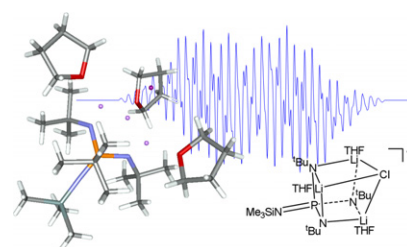


Heikki M. Tuononen, Tristram Chivers,
Andrea Armstrong, Chantall Fedorchuk,
René T. Boéré

J. Organomet. Chem. 692 (2007) 2705

Computational modeling of isotropic electron paramagnetic resonance spectra of doublet state main group radicals

Theoretical calculations have been used in combination with mathematical least-square-fit methods to aid in the analysis of some very complex experimental EPR spectra of inorganic main group radicals. This research has provided fundamental information about many new stable and persistent main group radicals that is not accessible by other methods.

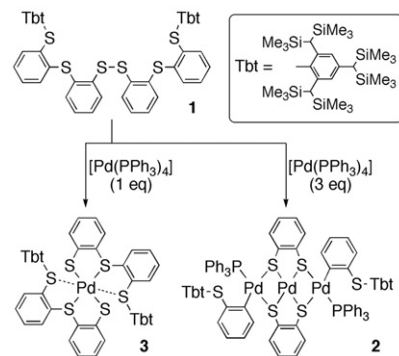


**Daisuke Shimizu, Nobuhiro Takeda,
Norihito Tokitoh**

J. Organomet. Chem. 692 (2007) 2716

Synthesis of mono- and trinuclear palladium(II) complexes via oxidative addition of a bulky hexathioether containing a disulfide bond to palladium(0)

Tripalladium(II) complex **2** was formed by the reaction of bulky hexathioether **1** with 3 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$ via the S–S and the unusual aryl C–S bond cleavages. On the other hand, the reaction of **1** with an equimolar amount of $[\text{Pd}(\text{PPh}_3)_4]$ affords mono-palladium(II) complex **3** having pseudo-octahedral structure.

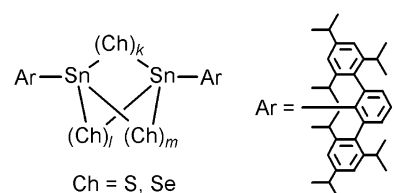


**Masaichi Saito, Hizuru Hashimoto,
Tomoyuki Tajima, Masatoshi Ikeda**

J. Organomet. Chem. 692 (2007) 2729

Synthesis and structures of polychalcogenadistannabicyclo[*k.l.m*]alkanes

Reaction of steric encumbered trichlorostannane with disodium sulfide or dilithium selenide gave 2,4-dimercapto-1,3,2,4-dithiadistannetane or tetraselenadistannabicyclo[2.1.1]hexane, respectively. Reactions of steric encumbered trihydrostannane with elemental chalcogens gave pentachalcogenadistannabicyclo[*k.l.1*]heptanes ($k = 2$ and 3).

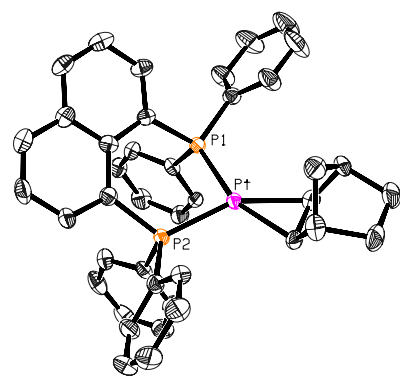


**Holm Petzold, Helmar Görls,
Wolfgang Weigand**

J. Organomet. Chem. 692 (2007) 2736

A simple and efficient synthesis of bis-phosphine platinum(0) complexes with various P–Pt–P angles

Improved syntheses of a series of $[(\text{L})_2\text{Pt}(\eta^2\text{-nb})]$ (**4**)–(**8**) ($\text{L} = \text{PPh}_3$, 1/2 dpp(*o*-xyl), 1/2 dppb, 1/2 dppbe, 1/2 dppn) complexes are described. The reactivity of $[(\text{dppn})\text{Pt}(\eta^2\text{-nb})]$ with the spirocyclohexyl-1,2,4-trithiolane **12** and the sterically hindered 2,2,4,4-tetramethyl-3-thioxocyclobutanone **13** was tested.

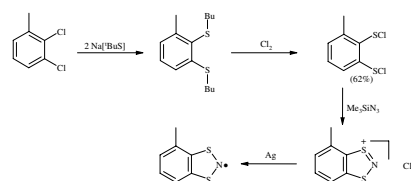


**Antonio Alberola, Rebecca J. Collis,
Robert J. Less, Jeremy M. Rawson**

J. Organomet. Chem. 692 (2007) 2743

New synthetic pathways into dithiazolyl radicals: Preparation and characterisation of 3'-methyl-benzo-1,3,2-dithiazolyl, M'BDTA

A general three-step synthesis to a range of benzo-fused-1,3,2-dithiazolium salts bearing both electron-withdrawing (CN) and electron-donating (Me) groups is described.

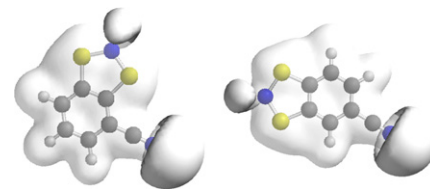


**Antonio Alberola, Jonathan Burley,
Rebecca J. Collis, Robert J. Less,
Jeremy M. Rawson**

J. Organomet. Chem. 692 (2007) 2750

Structural control of dithiazolyl radicals: Case studies on 3'- and 4'-cyano-benzo-1,3,2-dithiazolyl, $\text{NCC}_6\text{H}_3\text{S}_2\text{N}$

Dithiazolyl radicals with π -stacking motifs have attracted particular interest because of their ability to exhibit spin-switching between diamagnetic distorted π -stacks and paramagnetic regular π -stacked structures through a solid state phase transition. Previous studies indicate that inclusion of electronegative heteroatoms into the backbone favours lamellar structures. This methodology has been extended to the synthesis and characterisation of the title compound, 4'-cyanobenzo-1,3,2-dithiazolyl (4-NCBDTA).

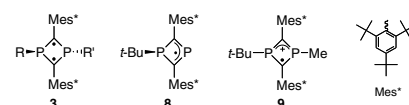


**Shigekazu Ito, Manabu Kikuchi,
Hiroki Sugiyama, Masaaki Yoshifuji**

J. Organomet. Chem. 692 (2007) 2761

Synthesis and properties of air-stable 1,3-diphosphacyclobutane-2,4-diyls and the related compounds

Reactions of a kinetically stabilized phosphalkyne ($\text{Mes}^*\text{C}\equiv\text{P}$; $\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) with lithium reagents and electrophiles afford several 1,3-diphosphacyclobutane-2,4-diyls of biradical type (**3**). Structures and properties of **3** indicate characters as singlet ground-state carbon-centered biradicals. We also succeeded in preparation and isolation of a novel P-heterocyclic air-stable neutral radical (**8**) and a P-heterocyclic cation radical (**9**).

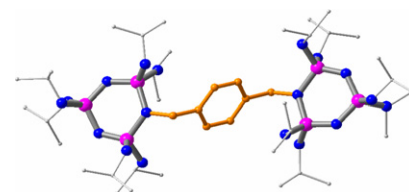


**Mark A. Benson, Ramamoorthy Boomishankar,
Dominic S. Wright, Alexander Steiner**

J. Organomet. Chem. 692 (2007) 2768

Cyclotriphosphazenes tethered together via N-ring centres with *ortho*-, *meta*- and *para*-xylylene linkers

Cyclotriphosphazenes $(\text{RNH})_6\text{P}_3\text{N}_3$ react with *ortho*-, *meta*- and *para*-derivatives of α,α' -dibromo xylene in 2:1 ratio to form salts of compositions $[\{(\text{RNH})_6\text{P}_3\text{N}_3\}_2\text{xy}]^+\text{Br}_2^-$. These contain dications consisting of two phosphazene rings, which are linked via ring N centres by a xylylene unit. This approach promises novel polycationic systems based on N-tethered phosphazenes.

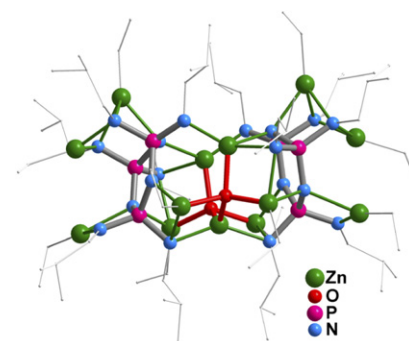


**Philip I. Richards,
Ramamoorthy Boomishankar,
Alexander Steiner**

J. Organomet. Chem. 692 (2007) 2773

Zinc oxide clusters encapsulated by organozinc phosphazenate assemblies

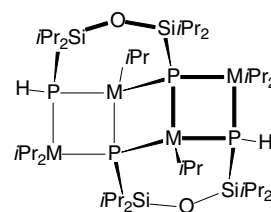
Reactions of diethylzinc with phosphazenes $(\text{RNH})_6\text{P}_3\text{N}_3$ and water in stoichiometric ratios yield zinc oxide clusters which are encapsulated by phosphazenate complexes. The coordination surface offered by the ethylzinc phosphazenate complexes controls the size and geometry of the zinc oxide clusters.



Carsten von Hänisch, Sven Stahl*J. Organomet. Chem.* 692 (2007) 2780

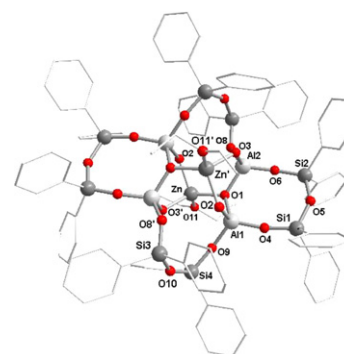
Metalated diphosphanyl siloxanes with polycyclic and polymeric structures

The polycyclic compounds **2** and **3** (see figure) have been obtained from the reaction of the diphosphanyl siloxane $O(SiPr_2PH_2)_2$ with $MiPr_3$ ($M = Ga, In$). The same diphosphanyl siloxane reacts with $n-BuLi$ under formation of a polymeric Li-P chain compound.

**2:** M = Ga**3:** M = In**Michael Veith, Hinka Hreleva-Carparrotti, Volker Huch***J. Organomet. Chem.* 692 (2007) 2784

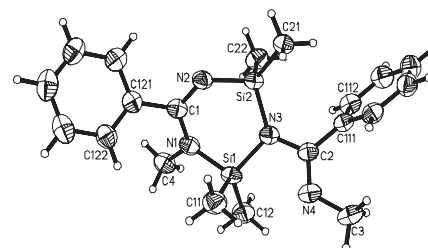
Two new metal derivatives of the alumosiloxane $[Ph_2SiO]_8[AlO(OH)]_4$: $[Ph_2SiO]_8[AlO_2(Na)]_4 \cdot 5(THF)$ and $[Ph_2SiO]_8[AlO(OH)]_2[AlO_2]_2 \cdot [Zn(OH)]_2 \cdot 2(OEt_2)$

The polycyclic alumosiloxane $[Ph_2SiO]_8[AlO(OH)]_4$ reacts with organometallic compounds to yield the new metal derivatives $[Ph_2SiO]_8[AlO_2(Na)]_4 \cdot 5(THF)$ and $[Ph_2SiO]_8[AlO(OH)]_2[AlO_2]_2[Zn(OH)]_2 \cdot 2(OEt_2)$.

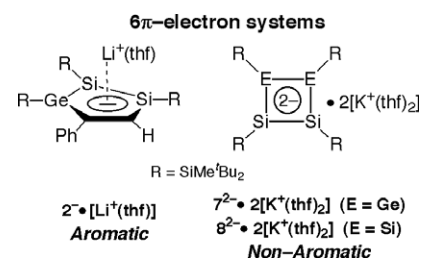
**Thomas Segmüller, Peter A. Schlüter, Markus Drees, Annette Schier, Stefan Nogai, Norbert W. Mitzel, Thomas Straßner, Hans H. Karsch***J. Organomet. Chem.* 692 (2007) 2789

Dianionic amidinates at silicon and germanium centers: Four-, six- and eight-membered rings

The formation of the different ring sizes in silicon- and germanium compounds is determined by steric and electronic effects, which have been investigated by a combination of experiments, X-ray structures and DFT calculations.

**Vladimir Ya. Lee, Kazunori Takanashi, Risa Kato, Tadahihiro Matsuno, Masaaki Ichinohe, Akira Sekiguchi***J. Organomet. Chem.* 692 (2007) 2800Heavy analogues of the 6π -electron anionic ring systems: Cyclopentadienide ion and cyclobutadiene dianion

The heavy analogues of the anionic 6π -electron systems, lithium 1,2-disila-3-germa-cyclopentadienide $2^- \cdot [Li^+(thf)]$, 1,2-disila-3,4-digerma- and 1,2,3,4-tetrasilacyclobutadiene dianions $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$, were synthesized by the reduction of the neutral precursors **1**, **3** and **4**, respectively. $2^- \cdot [Li^+(thf)]$, the heavy analogue of the cyclopentadienide ion, is an aromatic compound, whereas $7^{2-} \cdot 2[K^+(thf)_2]$ and $8^{2-} \cdot 2[K^+(thf)_2]$, the heavy analogues of the cyclobutadiene dianion, are both non-aromatic.

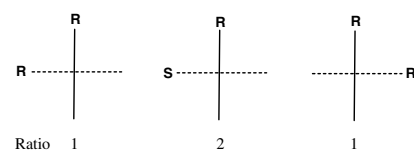


**Simon J. Coles, David B. Davies,
Michael B. Hursthouse, Adem Kılıç, Şule Şahin,
Robert A. Shaw, Aylin Uslu**

J. Organomet. Chem. 692 (2007) 2811

Stereogenic properties of spiranes combined with one or two equivalent conventional centres of chirality

Spiranes combined with two equivalent conventional centres of chirality are proven to exist as three racemic diastereoisomers by X-ray crystallography and/or ^{31}P NMR spectroscopy with added chiral solvating agent. The relative ratios (1:2:1) of the diastereoisomers observed by ^{31}P NMR spectroscopy are rationalised by analysis of the stereogenic properties of the formation reactions.

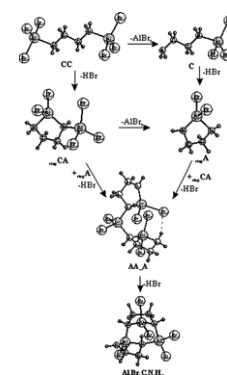


**C. Trinh, A.Y. Timoshkin, S.M. Matveev,
A.D. Misharev**

J. Organomet. Chem. 692 (2007) 2822

Ring and cage compounds from complexes of group 13 metal halides with ethylenediamine: Experiment and theory

Formation of gaseous ring and cage compounds by thermolysis of the complexes between group 13 metal halides MX_3 and ethylenediamine (en) has been observed experimentally by mass spectrometry method ($\text{M} = \text{Al}, \text{Ga}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) and studied theoretically for $\text{M} = \text{Al}, \text{X} = \text{Br}$. Existence of gaseous associates with molecular weight of 600–900 amu was observed for all studied systems. For $\text{M} = \text{Al}$, formation of carbon-free cubane-type clusters was evidenced.

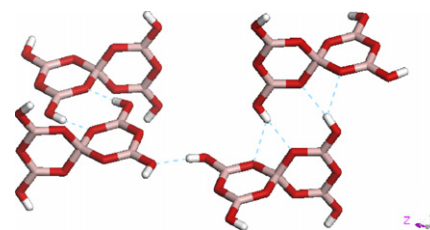


**Michael A. Beckett, Catherine C. Bland,
Peter N. Horton, Michael B. Hursthouse,
K. Sukumar Varma**

J. Organomet. Chem. 692 (2007) 2832

Supramolecular structures containing 'isolated' pentaborate anions and non-metal cations: Crystal structures of $[\text{Me}_3\text{NCH}_2\text{CH}_2\text{OH}][\text{B}_5\text{O}_6(\text{OH})_4]$ and $[\text{4-MepyH}, \text{4-Mepy}][\text{B}_5\text{O}_6(\text{OH})_4]$

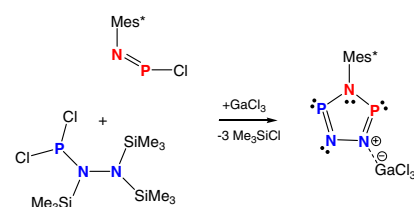
A pairwise 'step-like' bifurcated H-bond interaction is observed (right) in the supramolecular pentaborate framework of $[\text{4-MepyH}, \text{4-Mepy}][\text{B}_5\text{O}_6(\text{OH})_4]$ in addition to the more commonly observed pairwise 'planar' H-bond interactions (left).



Peter Mayer, Axel Schulz, Alexander Villinger
J. Organomet. Chem. 692 (2007) 2839

GaCl_3 -assisted [3+2] cycloaddition: A route to new binary PN-heterocycles

Starting from a [3+2] synthetic tool kit, a new triazadiphosphole has been isolated and fully characterized in a new synthetic approach called GaCl_3 -assisted [3+2] cycloaddition.

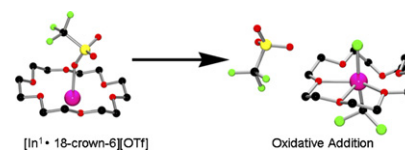


**Benjamin F.T. Cooper,
Christopher G. Andrews,
Charles L.B. Macdonald**

J. Organomet. Chem. 692 (2007) 2843

The insertion reactions of “crowned” indium(I) trifluoromethanesulfonate into carbon–chlorine bonds

The reaction of crown ether In^{I} complexes with certain chlorinated solvents results in the insertion of the In center into a carbon–chlorine bond.



Communication

Timothy J. Clark, Ian Manners

J. Organomet. Chem. 692 (2007) 2849

Transition metal-catalyzed dehydrocoupling of group 13–group 15 Lewis acid–base adducts

Lewis acid–base adducts of Groups 13 and 15 can undergo dehydrocoupling with both early and late transition metals and complexes thereof to yield rings, chains and macromolecules based on a framework of alternating B–N or B–P atoms. Evidence is also provided for Group 13 hydrides acting as poisons towards heterogeneous dehydrocoupling catalysts.

