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Special Issue dedicated to the memory of Professor Colin Eaborn

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Volume 19 Number 4

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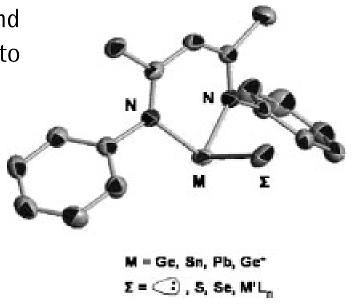

I. Saur, S. Garcia Alonso and J. Barrau*
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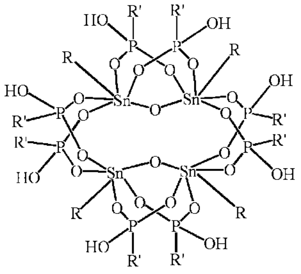
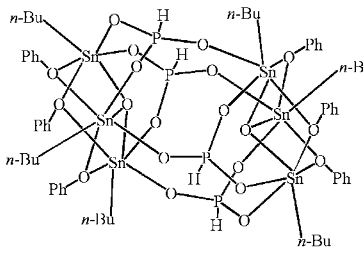
Recent progress in the assembly of monoorganotin(IV) phosphonates is reviewed.





V. Chandrasekhar* and K. Gopal
.... 429–436

Review: Monoorganotin(IV) phosphonates

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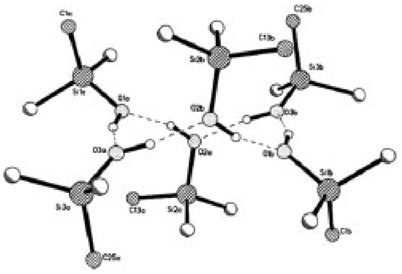
Section: Main Group Metal Compounds

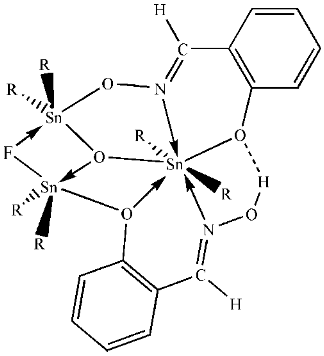
Ferrocenyldimethylsilanol, $FcSiMe_2OH$, $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, features a hydrogen-bonded, self-assembled, cyclohexameric supermolecule with a chair conformation.



H. K. Sharma, F. Cervantes-Lee, I. Haiduc and K. H. Pannell* 437–439

Short communication: Unprecedented self-assembled cyclic hexamer of ferrocenyldimethylsilanol, $[FcSi\ Me_2OH]_6$, $(Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4))$

An overview is given of the research performed by the authors at the Université Libre de Bruxelles and the Vrije Universiteit Brussel, including the kinetics, stereochemistry and mechanism of S_E2 reactions at a saturated carbon atom, the synthesis of chiral organotin compounds and their configurational and optical stability, the fluxionality of trigonal bipyramidal metal atoms and the stereochemistry of S_N2 reactions at tetrahedrally substituted atoms of the third, fourth or fifth period, the cytotoxicity of many series of organotin compounds and the structure and reactivity of organotin salicylaldoximate clusters.



M. Gielen*, M. Biesemans and R. Willem 440–450

Organotin compounds: from kinetics to stereochemistry and antitumour activities

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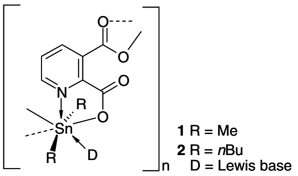
Dimethyl- and di-*n*-butyltin(IV) 2,3-pyridinedicarboxylate have been characterized both in solution (^1H, ^{119}Sn NMR) and in the solid state (X-ray crystallography). Significant differences have been found for their structural and electronic properties in comparison to their analogs with phthalate as ligand.



R. García-Zarracino and H. Höpfl* 451–457

Structural characterization of dimethyl- and di-n-butyltin(IV) 2,3-pyridinedicarboxylate in solution and in the solid state

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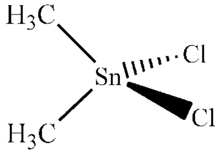
In 1998, the US Environmental Protection Agency launched the High Production Volume (HPV) Challenge Program, which called for chemical manufacturers to voluntarily commit to fill gaps in basic screening-level hazard data for high volume chemicals they manufacture and to make the data available to the regulatory community as well as the public. Companies could sponsor chemicals individually or, if there were multiple manufacturers, companies could join together to form consortia to jointly sponsor work. The organotin industry, through the Stabilizer Task Force of ORTEPA, volunteered 27 organotin and related inorganic compounds for this program. This paper addresses setting up the industry effort, securing committed funding, sharing of existing data, establishing the test plans, contracting for the testing and administering the testing. It also provides an update as to where industry is in meeting its obligations.



J. M. Batt* 458–464

The organotin industry rises to the HPV Challenge

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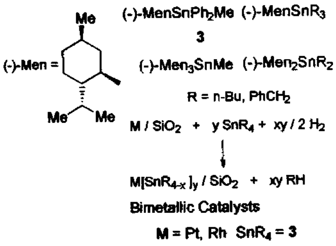
Section: Materials, Nanoscience and Catalysis

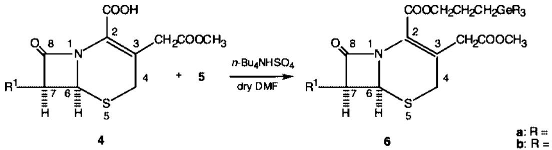


The synthesis of organotin compounds with chiral (−)-menthyl ligands attached to the tin atom and free of epimerization by-products is reported. Also described is the preparation of some new bimetallic catalysts prepared by modifying silica-gel-supported platinum and rhodium with a chiral organotin, as well as some hydrogenation reactions using these catalysts. Full ^1H, ^{13}C, and ^{119}Sn NMR spectra of the new organotins are reported.

M. B. Faraoni, A. D. Ayala, V. Vetere, M. L. Casella, O. A. Ferretti, J. C. Podestá* 465–472

Synthesis of chiral organotins suitable for the preparation of asymmetric heterogeneous catalysts

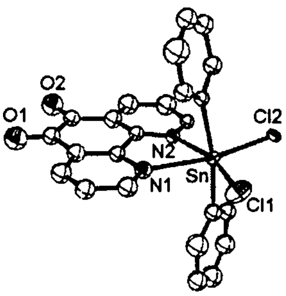
Section: Main Group Metal Compounds



A cepham, cephalothin (4), was modified with germanium-containing moieties. Their structures were confirmed chiefly based on electrospray ionization mass spectrometry and NMR spectroscopy and their antibacterial properties were tested. None of these exhibited activity strong enough to be used as a medicine.

Y. Takeuchi*, Y. Kase and Y. Imafuku 473–478

Synthesis and characterization of several cephalothin derivatives modified with germanium-containing moieties

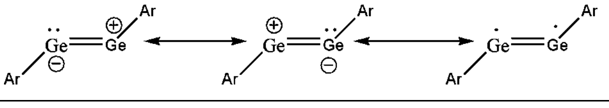


An evaluation of the PM3 level of calculation applied to organotin compounds has been carried out, by comparing calculated structures for 19 compounds with published experimental data. The method was also applied to the new $[Ph_2SnCl_2(1,10\text{-phenanthroline-5,6-dione})]\cdot 2Me_2CO$ complex, whose crystal structure is also described.

R. B. de Alencastro, J. A. S. Bomfim*, C. A. L. Filgueiras, R. A. Howie and J. L. Wardell 479–487

Evaluation of PM3 calculations applied to organotin compounds: crystal structure of $[Ph_2SnCl_2(1,10\text{-phenanthroline-5,6-dione})]\cdot 2Me_2CO$

The syntheses and reactivity of germanium, tin, and lead analogues of alkynes is summarized. Heavier group 14 'alkynes' are stabilized by bulky terphenyl ligands and are thermally robust crystalline solids; however, they are extremely reactive, with reactivity decreasing in the order Ge > Sn > Pb. Spectroscopy and reactivity patterns suggest that the germanium species, in particular, has considerable diradical character. This hypothesis is also supported by preliminary density functional theory calculations.



P. P. Power* 488–493

Synthesis and some reactivity studies of germanium, tin and lead analogues of alkynes

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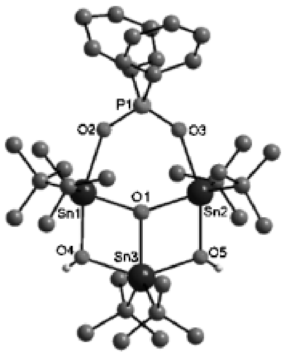
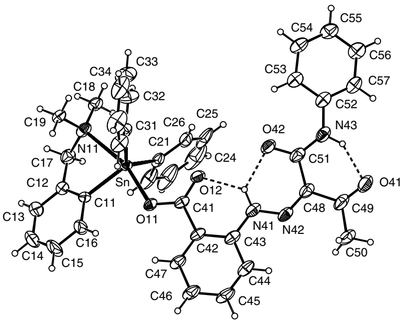
Recent advances in the chemistry of organotin triflates and related organotin cations are reviewed. Applications in synthesis and catalysis are briefly discussed.



J. Beckmann* 494–499

Hypercoordinated organotin triflates

Eight complexes of azo dyes and the [(2-dimethylaminomethyl)phenyl](R_2)tin(IV) (R = is Ph or *n*-Bu) moiety were prepared and their NMR, ESI-MS, IR and UV–VIS spectra measured and X-ray structure determined. The compounds reveal the same structure in chloroform solution and in the solid state. Four compounds exist in the hydrazone tautomeric form. The central tin atoms in all compounds exist in slightly distorted *trans*-trigonal bipyramidal geometry. The *in vitro* antifungal activity of the compounds studied was comparable to similar organotin(IV) compounds and antifungal drugs in clinical use.



P. Novák, A. Lyčka, I. Císařová, V. Buchta, L. Silva, L. Kolářová, A. Růžička* and J. Holeček** 500–509

Structure of azo dye organotin(IV) compounds containing a C,N-chelating ligand, part II, and their in vitro antifungal activity

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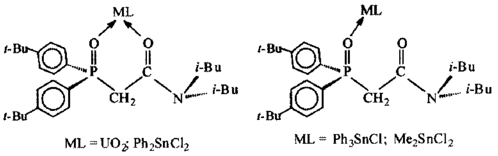
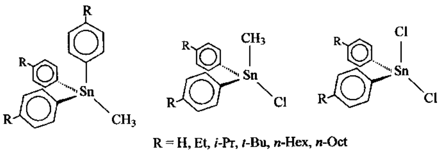
The actinide complexing agent di(*p*-*tert*-butylphenyl)-*N*,*N*-di-(*iso*-butyl)carbamoylmethylphosphine oxide (**1**) has been used to form a series of complexes with Ph_3SnCl (**3**), Me_2SnCl_2 (**4**), and Ph_2SnCl_2 (**5**). In the solid state the ligand is either monodentate (**3, 4**), binding through the PO unit, or bidentate (**5**), chelating via the PO and CO groups. In solution they are all monodentate. The uranyl complex is also reported where the ligand is bidentate in both solid state and solution.



R. N. Kapoor, P. Guillory, L. Schulte, F. Cervantes-Lee, I. Haiduc, L. Parkanyi and K. H. Pannell* 510–517

*Di(p-*tert*-butylphenyl)-*N,N*-di-(*iso*-butyl) carbamoylmethylphosphine oxide and its organotin and uranyl adducts: structural and spectroscopic characterization*

A series of new arylmethyl organotins, Ar_3MeSn, $Ar_2SnMeSnCl$ and $ArMeSnCl_2$, are reported. The synthetic method commences with the formation of the triarylmethyl tin compounds from $MeSnCl_3$ via Grignard methods followed by sequential aryl group cleavage by $HCl–Et_2O$. The $Ar_2MeSnCl$ and previously reported $ArMe_2SnCl$ compounds were evaluated against *Staphylococcus aureus*.



R. N. Kapoor, P. Apodaca, M. Montes, F. Gomez and K. H. Pannell* 518–522

Mixed aryl–alkyl organotin compounds, $Ar_nMeSnCl_{3-n}$ *(Ar =* RC_6H_4*, R = H, ethyl, i-propyl, t-butyl; n-hexyl, n-octyl) and the effect of R upon antibiotic activity*

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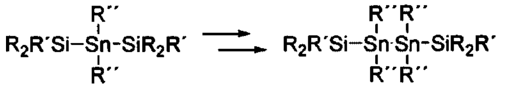


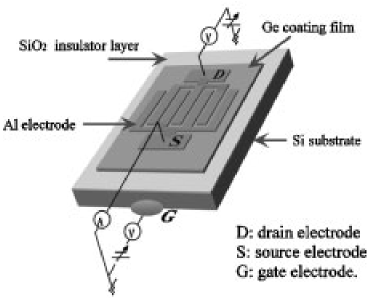
$$R_2R'Si{-}\overset{R''}{\underset{R''}{Sn}}{-}SiR_2R' \longrightarrow R_2R'Si{-}\overset{R''}{\underset{R''}{Sn}}{-}\overset{R''}{\underset{R''}{Sn}}{-}SiR_2R'$$

Bis(triorganosilyl)diorgano-stannanes or -distannanes can selectively be prepared by Wurtz-type coupling reactions. In addition, metallation of $(R_2R'Si)_2SnR''_2$ yields the respective monosilylated potassium stannides, from which the corresponding distannanes are readily obtained from oxidative coupling reactions.

R. Fischer, T. Schollmeier, M. Schürmann and F. Uhlig* 523–529

Syntheses of novel silylsubstituted distannanes

The field-effect transistor fabricated by a coating technique using organosoluble germanium nanoclusters shows amplification properties.



A. Watanabe*, F. Hojo and T. Miwa 530–537

Field-effect transistor based on organosoluble germanium nanoclusters

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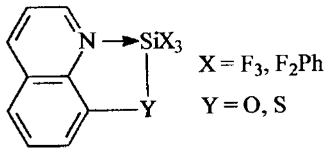

The protodesilylation of phenyltrifluorosilane with 8-hydroxy- and 8-mercapto-quinoline NC_9H_6YH (Y : O, **1a**; S, **1b**) affords the novel intramolecular pentacoordinate silanes (N ⟶ Si) 8-(trifluorosiloxy)- and (N ⟶ Si) 8-(trifluorosilylthio)-quinoline respectively. (N ⟶ Si) 8-(Phenyldifluorosiloxy)- and (N ⟶ Si) 8-(phenyldifluorosilylthio)-quinolines prepared by the transsilylation reaction of trimethylsilyl derivatives of heterocycles **1a** and **1b** by phenyltrifluorosilane possess a similar pentacoordinate structure.

M. G. Voronkov*, O. M. Trofimova, N. F. Chernov, A. I. Albanov, N. N. Chipanina and E. A. Grebneva 538–541

Reaction of phenyltrifluorosilane with 8-hydroxy- or 8-mercapto-quinoline and their derivatives as a route to new heterocyclic compounds of pentacoordinate silicon

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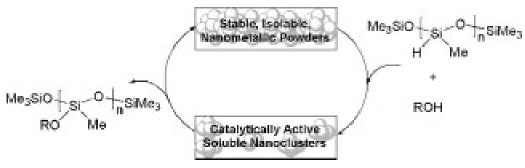
Section: Materials, Nanoscience and Catalysis



A new synthetic route to catalytically active, stable and isolable palladium nanocomposites is disclosed. The utility of such nanocomposites is demonstrated by the investigations of their activity as a recyclable catalyst for macromolecular grafting of polyhydrosiloxane.

B. P. S. Chauhan*, J. S. Rathore and N. Glloxhani 542–550

First example of 'palladium-nanoparticle'-catalyzed selective alcoholysis of polyhydrosiloxane: a new approach to macromolecular grafting

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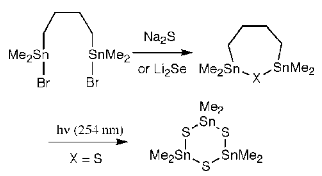
Section: Main Group Metal Compounds



1,2,7-Chalcogenadistannacycloheptanes were synthesized by the reactions of 1,4-bis(bromostannyl) butane with appropriate chalcogenation reagents. Irradiation of the 1,2,7-thiadistannacycloheptane with a low-pressure mercury lamp (254 nm) gave 1,3,5,2,4,6-trithiatristannin. Irradiation of 1,3,5,2,4,6-trithiatristannin with a low-pressure mercury lamp in the presence of either cyclotrisiloxane or 2,3-dimethyl-1,3-butadiene gave a complex mixture.

M. Saito*, K. Iso, K. Yamada, S. Nakano and M. Yoshioka 551–554

Synthesis and photochemical reactions of 1,2,7-chalcogenadistannacycloheptanes

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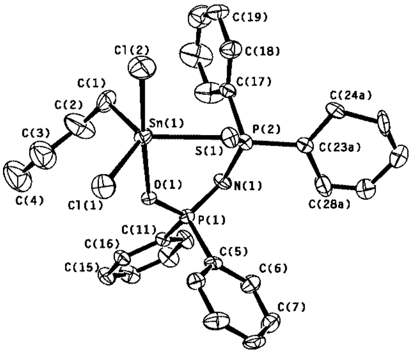
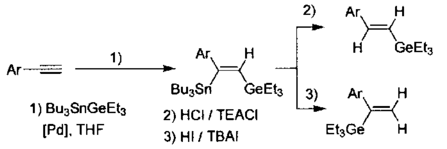
$BuSnCl_2[(OPPh_2)(SPPh_2)N]$ (**1**) and $BuSnCl[(OPPh_2)(SPPh_2)N]_2$ (**2**) have been prepared and their behaviour in solution and solid state was investigated by multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy and single-crystal X-ray diffraction. Variable-temperature ^{31}P NMR studies indicate the presence of various isomers for **2** in solution. The molecular structure in solid state features 5- and 6-coordinated metal atoms in **1** and **2**, respectively, as a result of the monometallic biconnective behaviour of the monothioimidodiphosphinato moieties. Preliminary results on the *in vitro* antibacterial activity are reported.



Adina Rotar, Anca Silvestru, Cristian Silvestru*, John E. Drake, Michael B. Hursthouse, Mark E. Light, Liana Bunaciu and Petre Bunaciu 555–562

Structure and in vitro antibacterial activity of $BuSnCl_{3-n}[(OPPh_2)(SPPh_2)N]_n$ (n = 1, 2)

Protodemetallation of (*Z*)-germyl(stannyl)ethenes gives *trans*-germylethenes or 1-aryl-1-germylethenes depending on the acid used. The reaction with HCl/TEACl (tetraethylammonium chloride) gives the former ethenes, while the use of HI/TBAI(tetrabutylammonium iodide) produces 1-aryl-1-germylethenes selectively.



Taichi Nakano*, Yoshiya Senda, Kayo Fukaya, Naoyuki Sugiuchi, Shinobu Niimi, Takanori Endoh and Yutaka Takahashi 563–569

Acid-dependent selective formation of trans-aryl(germyl)ethenes or 1-aryl-1-germylethenes by the protodestannylation of (Z)-germyl(stannyl)ethenes

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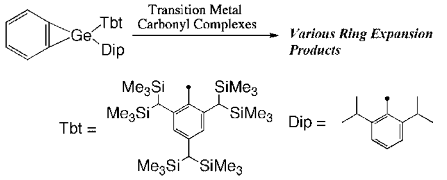
An overcrowded, diaryl-substituted germacyclopropabenzene underwent unique reactions with transition metal carbonyl complexes to give a variety of Ge-containing cyclic compounds, such as Fischer-type carbene complexes, a germacyclobutabenzene, and a germacyclobutanone, depending on the kinds of reactants.



Tomoyuki Tajima, Takayo Sasaki, Takahiro Sasamori, Nobuhiro Takeda and Norihiro Tokitoh* 570–577

Reactivities of germacyclopropabenzene toward some transition metal carbonyl complexes

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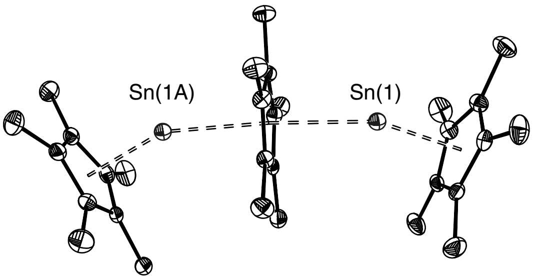
Triple-decker tin and lead cations can be prepared by the addition of $[(\eta^5\text{-}C_5Me_5)M]^+$ cations (M = Sn, Pb) to the appropriate decamethylmetallocene.



A. H. Cowley*, J. N. Jones, and C. L. B. Macdonald 578–582

Triple-decker tin and lead cations