Applied Organometallic Chemistry

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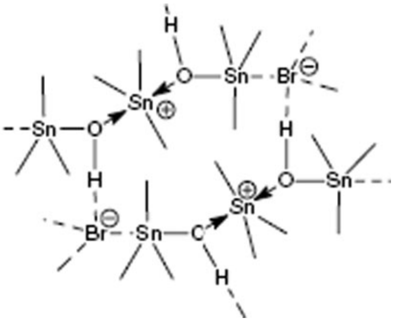
Section: Main Group Metal Compounds

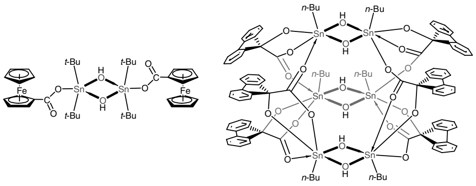
Supramolecular self-assembly through hydrogen bonds, dative (coordinate) bonds, soft-soft (secondary bond) and pi-bond interactions as bonding motifs available for supramolecular self-assembly in organotin and organolead chemistry is illustrated.



I. Haiduc* 476–482

Supramolecular aspects of tin and lead chemistry

Compounds containing the distannoxane core $[Sn_2(\mu\text{-}OH)_2]$ are reviewed. Synthesis and structural aspects of these compounds are summarized in this article.



V. Chandrasekhar*, P. Singh and K. Gopal 483–503

Organotin compounds containing four-membered distannoxane $[Sn(\mu\text{-}OH)]_2$ units

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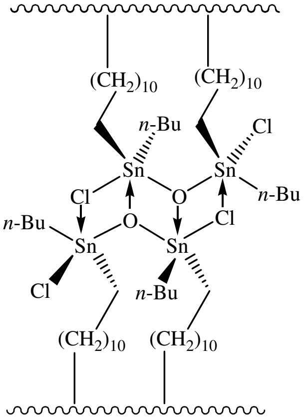
The catalytic properties of a cross-linked polystyrene-grafted diorganotin dichloride and chlorodistannoxane are compared in the transesterification reaction of ethyl acetate and *n*-octanol, as well as in the ring-opening polymerization (ROP) of ε-caprolactone. Moreover, ^{119}Sn hr-MAS NMR and ^{117}Sn CP-MAS NMR spectroscopy appear to be complementary techniques for the assessment of the tin(IV) functionality of the grafted tetraalkyldichlorodistannoxane showing a dimeric ladder arrangement.

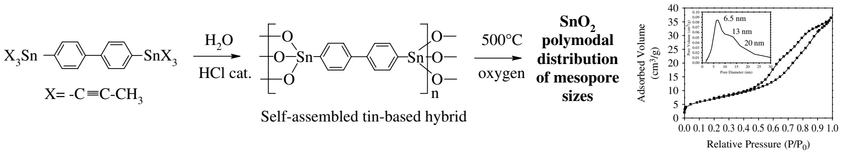


K. Poelmans, V. Pinoie, I. Verbruggen, M. Biesemans* , G. Van Assche, G. Deshayes, P. Degée, P. Dubois and R. Willem 504–513

Catalytic properties of cross-linked polystyrene grafted diorganotins in a model transesterification and the ring-opening polymerization of ε-caprolactone

---

Hydrolysis of α,ω-bis(trialkynyltin) compounds in which the two tin atoms are bridged through a rigid or a semi-rigid linker provides self-assembled tin-based hybrid materials. Calcination of these materials leads to nanocrystalline tin dioxide materials showing, in some cases, an unusual polymodal distribution of mesopore sizes.



T. Toupance*, M. de Borniol, H. El Hamzaoui and B. Jousseaume 514–520

Alkynylorganotins, versatile precursors of class II hybrid materials

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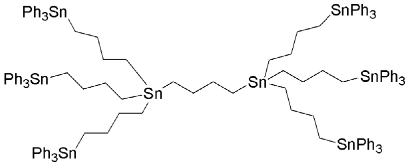
Alkylation of $Cl_3Sn(CH_2)_nSnCl_3$ ($n = 4, 5$) with $BrMg(CH_2)_2CH{=}CH_2$ affords $(CH_2{=}CHCH_2CH_2)_3Sn(CH_2)_nSn(CH_2CH_2CH{=}CH_2)_3$, which undergoes hydrostannylation with Ph_3SnH forming $[Ph_3Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_3]_3$. Both compounds are converted by HCl to $[ClPh_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2Cl]_3$, then by $LiAlH_4$ to $[HPh_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2H]_3$ and finally by $CH_2{=}CHCH_2OH$ yielding $[HO(CH_2)_3Ph_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2(CH_2)_3OH]_3$.



Y. Aksu, S. Aksu and H. Schumann* 521–530

Synthesis and characterization ofα, ω-bis [tri - (w - triphenylstannyl) butylstannyl] alkanes as starting materials for organotin dendrimers

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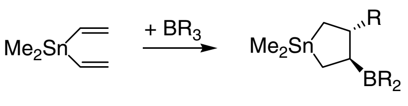
Dimethyl(divinyl)tin reacts with triorganoboranes BR_3 by intermolecular 1,1-organoboration, followed by ring closure via intramolecular 1,1-organoboration to give boryl-substituted stannolanes. With diethylborane hydroboration takes place, also followed by ring closure via cleavage of the Sn–C=bond, and the mechanism was confirmed using di-2-propenyltin compounds.



B. Wrackmeyer* and O. L. Tok 531–538

First 1,1-organoboration reactions of vinyltin compounds—a route to boryl-substituted stannolanes and organo-substituted stannol-3-enes

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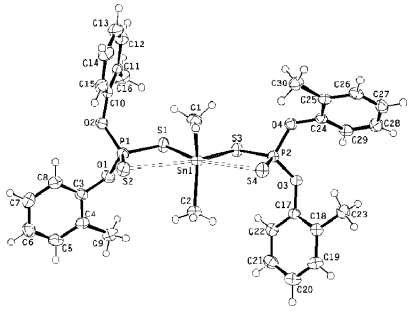
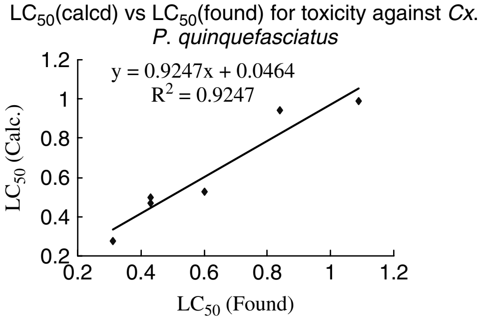
Organotin(IV) complexes of the type, $R_2Sn[S_2P(OR')_2]_2$ (where R = Me, Bu and R′ = *o*-, *m*-, *p*-C_6H_4Me) were obtained by the reaction of Me_2SnCl_2 or Bu_2SnCl_2 with ammonium salts of the corresponding *O*, *O*′-ditolyl dithiophosphates. Crystal structures for $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ and $Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ were determined. The geometry around the tin atom in both molecules may be described as having skew-trapezoid bipyramidal geometry.



J. E. Drake, C. Gurnani, M. B. Hursthouse, M. E. Light, M. Nirwan and R. Ratnani* 539–544

*Synthesis and spectroscopic characterization of dimethyl/di(*n*-butyl)tin(IV)bis(*O,O*′-ditolyl dithiophosphate) complexes. Crystal structures of $Me_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$ and* n*-$Bu_2Sn[S_2P(OC_6H_4Me\text{-}o)_2]_2$*

A series of triorganotin 2,2,3,3-tetramethylcyclopropanecarboxylates, where R = methyl, ethyl, *n*-propyl, *n*-butyl, phenyl and cyclohexyl, have been synthesized. Based on the spectroscopic results, all the complexes, with the exception of the tricyclohexyl compound, were found to be five-coordinated, while the tri-cyclohexyltin derivative was determined to be four-coordinated in the solid state. NMR studies indicate that all the complexes are four-coordinated in solution. Larvicidal results indicated that this series of triorganotins are effective against three species of mosquito larvae. In addition, quantitative structure–activity relationships (QSARs) were also developed for each species of larvae.



X. Song, A. Zapata, J. Hoerner, A. C. de Dios, L. Casabianca and G. Eng* 545–550

Synthesis, larvicidal, QSAR and structural studies of some triorganotin 2,2,3,3-tetramethylcyclopropanecarboxylates

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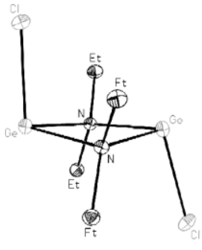
New stable amidogermanium(II) and -tin(II) chlorides $R_2N{-}E^{14}{-}Cl$ [E^{14} = Ge, R = Et (**1**), E^{14} = Sn, R = Me (**2**)] have been synthesized and their crystal structures have been determined by X-ray diffraction analysis. Both structures of **1** and **2** represent new structural motifs for amidogermanium(II) and -tin(II) chlorides, respectively. The electronic structures of **1** and **2** were studied using the DFT.



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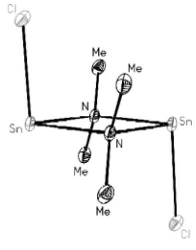

2

V. N. Khrustalev*, I. V. Glukhov, I. V. Borisova and N. N. Zemlyansky 551–556

New stable germylenes, stannylenes, and related compounds. 8. Amidogermanium(II) and -tin(II) chlorides $R_2N{-}E^{14}{-}Cl$ (E^{14} = Ge, R = Et; E^{14} = Sn, R = Me) revealing new structural motifs

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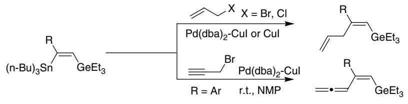
Stereodefined synthesis of an unprecedented family of vinylgermanes bearing an allyl group, (*E*)-2-aryl-1-germylalka-1,4-dienes, or an allenyl group, (*E*)-4-aryl-5-germylpenta-1,2,4-trienes, via a cross-coupling reaction of (*Z*)-germyl(stannyl) ethenes with the respective allyl halide (Br, Cl) and propargyl bromide is described.



K. Kato, Y. Senda, Y. Makihara, T. Kojima, H. Kurihara, Y. Takahashi and T. Nakano* 557–571

*Synthesis of novel stereodefined vinylgermanes bearing an allyl group or an allenyl group: (*E*)-2-aryl-1-germylalka-1,4-dienes and (*E*)-4-aryl-5-germylpenta-1,2,4-trienes*

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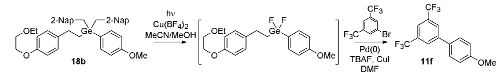
Bis(2-naphthylmethyl)aryl germane **18b** is identified as a ‘safety-catch’ precursor for Pd(0) catalysed cross-coupling with aryl bromides activated by TBAF in DMF. The 2-naphthylmethyl substituents are removed *via* photolytic oxidation in the presence of $Cu(BF_4)_2$.



A. C. Spivey*, C. J. G. Gripton, J. P. Hannah, C.-C. Tseng, P. de Fraine, N. J. Parr and J. J. Scicinski **572–589**

The development of a ‘safety-catch’ arylgermane for biaryl synthesis by palladium-catalysed germyl-stille cross-coupling

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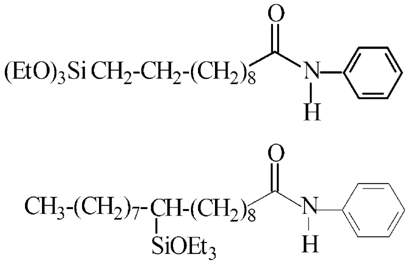
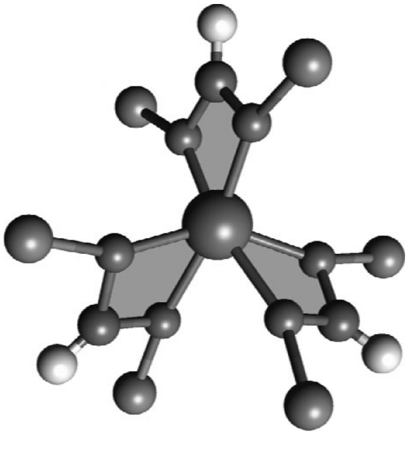
New silylated fatty acid *N*-phenyl amides have been synthesized and characterized. According the position of the double bond (terminal or internal), hydrosilylation reactions were performed using transition metal catalysis or radical initiation sequence.



A. El Kadib, N. Katir, A. Castel*, F. Delpech and P. Rivière* ... **590–594**

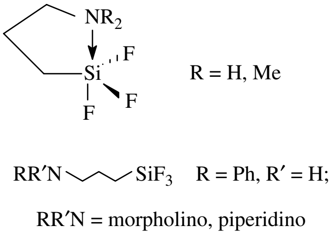
Hydrosilylation of unsaturated fatty acid N-phenyl amides

The hexacoordinate $M(Me_3SiNCHNSiMe_3)_3$ (M=Al,Ga) metal amidinate compounds incorporating the bidentate $[Me_3SiNCHNSiMe_3]^{1-}$ ligand were synthesized for the first time. X-ray diffraction revealed molecular structures in which the ‘amidinate’ groups form three M–N–C–N ‘propeller paddles’ terminated by six $SiMe_3$ groups, surrounding the central metal atom. The Al–N–C–N ring and the two corresponding Si atoms lie virtually on the same plane within each propeller unit.



C. Ritter, A. V. G. Chizmeshya, T. L. Gray and J. Kouvetakis* **595–600**

Synthesis and structures of $M(Me_3SiNCHNSiMe_3)_3$ (M=Al,Ga) via reactions of M-hydrides with $Me_3SiNCNSiMe_3$



N-substituted (3-aminopropyl)trifluorosilanes $RR'NCH_2CH_2CH_2SiF_3$ were synthesized in order to investigate the effect of the substituents at the nitrogen atom on the N→Si intramolecular interaction. Compounds were prepared by the reaction of KF with $F_3BN(CH_2CH_2CH_2SiF_3)RR'$ or $H(RR'NCH_2CH_2CH_2SiF_4)$. The structure of the compounds was confirmed by ^1H, ^{13}C, ^{19}F, ^{29}Si NMR and IR spectroscopy. The spectral data suggest pentacoordination at silicon in the compounds with R = R′ = H, Me resulting from a relatively strong N → Si intramolecular bonding.

M. G. Voronkov*, N. F. Chernov, A. I. Albanov, O. M. Trofimova, Y. I. Bolgova, E. A. Grebneva **601–603**

(3-Aminopropyl)trifluorosilanes and their N-substituted derivatives

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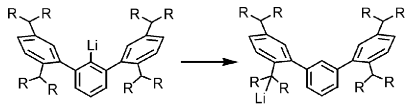
A novel bulky aryllithium, 2,6-bis{2, 5-bis[bis(trimethylsilyl)methyl]phenyl}phenyllithium (BbspLi), was synthesized. Reactions of BbspLi **5** with Group 14 electrophiles such as stannous chloride with carbon tetrachloride or tetrachlorometallanes gave fluorene **6**. Reaction of BbspLi with carbon tetrachloride gave benzyl chloride **8**, which converted to **6** under acidic conditions. Thus, BbspLi **5** isomerized to the corresponding benzyl anion **10**, which underwent halophilic reactions with Group 14 electrophiles to give fluorene **6** via the benzyl chloride intermediate **8**.



R=SiMe$_3$

BbspLi

M. Saito*, Y. Okuyama, T. Tajima, D. Kato and M. Yoshioka 604–611

Synthesis and reactions of a novel bulky aryllithium