Main Group Chemistry, 1996, Vol. 1, pp. 283–286 Reprints available directly from the publisher Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association) Amsterdam B.V. Published in The Netherlands under license by Gordon and Breach Science Publishers SA Printed in Canada

## **Index Abstracts**

The reaction of allyltributylgermane with organic halides in the presence of azobisisobutyronitrile or dichlorotris (triphenylphosphine) ruthenium (II) brought about allylation of organic halides to give the corresponding products in moderate yields. The reaction using AIBN as an initiator may be concluded to proceed through a  $S_{H\nu}$  mechanism.

Taichi Nakano, Masanori Kosugi, and Toshihiko Migita

The Reaction of Allyltributylgermane with Organic Halides

287-289

 $R-X + CeBu_3 \xrightarrow{Cat.} R + Bu_3GeX$ 

 $R: CCl_3, CHCl_2, CH_2CN, CH_2COOEt, CHMeCOOMe, CHEtCOOEt$ 

The monomeric subvalent indium(I) complex supported by ligation of the *tris* (3, 5-di-*t*-butylpyrazolyl)hydroboran ligand,  $(Tp^{Bu'_2}]In$ , undergoes oxidative-addition reactions with elemental I<sub>2</sub> and S<sub>8</sub> to give the indium (III) complexes  $[Tp^{Bu'_2}]InI_2$  and  $[Tp^{Bu'_2}]In(\eta^2-S_4)$  (shown) respectively.



52

Matthew C. Kuchta and Gerard Parkin

Oxidative-Addition Reactions of a Monomeric Indium(I) Complex Supported by Tris (3, 5-di-*t*-butylpyrazolyl)hydroborato Ligation,  $[Tp^{Bu'_2}]In$ : The Syntheses and Structures of  $[Tp^{Bu'_2}]InI_2$  and  $[Tp^{Bu'_2}]In(\eta^2-S_4)$ 

291-295

The zinc complex  $[Pim^{Pr'2}] Zn(NO_3)_2$ shown has been synthesized by the reaction of *tris*[2-(1,4-diisopropylimidazoyl)] phosphine  $[Pim^{Pr'_2}]$  with  $Zn(NO_3)_2$  6(H<sub>2</sub>O). Comparison of the structure of  $[Pim^{Pr'_2}]Zn(NO_3)_2$  with its more heavily substituted analogue  $\{[Pim^{Pr',Bu'}]Zn(NO_3)\}(NO_3)$  demonstrates the rather dramatic structural consequences of replacing the *t*-butyl substituents in the 4-positions of the imidazolyl moieties with isopropyl groups.



Clare Kimblin, William E. Allen, and Gerard Parkin

The Synthesis and Structure of Tris[2-(1,4-diisopropylimidazolyl)] phosphine Zinc Nitrate, [Pim<sup>Pr2</sup>]-Zn(NO<sub>3</sub>)<sub>2</sub>: Structural Consequences of *t*-Butyl *versus* Isopropyl Substitution in Tris(imidazolyl) phosphine Zinc Complexes

The title compound,  $(2,6-\text{Mes}_2\text{C}_6\text{H}_3)_2$ InBr, I, is prepared by an interesting disproportionation of  $\text{In}_2\text{Br}_4 \cdot 2\text{TMEDA}$  in the presence of  $(2,6-\text{Mes}_2\text{C}_6\text{H}_3)$ Li(Mes = 2, 4,  $6-\text{Me}_3\text{C}_6\text{H}_2$ ) in toluene. The structure of I is sufficiently distorted from the expected trigonal planar geometry by the two bulky ligands such that it represents the first example of a three-coordinate indium complex assuming a T-shaped conformation.



Xiao-Wang Li, Gregory H. Robinson and William T. Pennington

Disproportionation of Low Valent Indium Bromide: Synthesis and Molecular Structure of Bis (2, 6-dimesitylphenyl) indium bromide, (2, 6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> In Br (Mes = 2, 4, 6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>). When Does Trigonal Planar Become T-Shaped?

301-307

The structure of the dimeric tristannoxane  $[(N_3)Bu_2Sn(Bu_2SnO)_2N_3]_2$  has been characterised crystallographically and represents the first structurally authenticated tristannoxane without chelating ligands on every metal.

Reaction of  $ArS_3N_2Ar$  [Ar = Ph, p- $O_2N.C_6H_4$ -], with (NSCl)<sub>3</sub> leads to the chain extended products. [ $ArS_4N_3Ar$ ] Cl. Metathesis with AgAsF<sub>6</sub> yields the hexafluoroarsenate (V) salts, [ $ArS_4N_3Ar$ ] [AsF<sub>6</sub>], the structure of the *para*-nitrophenyl derivative is reported. In comparison, o- $O_2N.C_6H_4.S_3N_2.C_6H_4$ . NO<sub>2</sub> does not react with (NSCl)<sub>3</sub> alone, but chain lengthening can be achieved in the presence of AgAsF<sub>6</sub>.



M. Hill, M. F. Mahon and K. C. Molloy

The Structure of 1,5-Diazido-1,1,3,3,5,5-hexabutyltristannoxane

309-315

Judith A. K. Howard, Ian Lavender, Jeremy M. Rawson and Elizabeth A. Swain

Use of  $(NSCl)_3$  as a Chain-Building Reagent, I: Reaction of  $ArS_3N_2Ar$ with  $(NSCl)_3$  in the Presence of AgAsF<sub>6</sub> to Form the Chain-Lengthened Product,  $[ArS_4N_3Ar][AsF_6]$ 



The third–order nonlinear optical susceptibilities ( $\chi^{(3)}$ ) of thioxanthen–9– one (**3**) and its derivatives carrying 1,4-dimethyl (**5**), 2, 4-dimethyl (**6**), 1, 4dimethoxy (**7**), or 2-methoxy-7-nitro (**8**) substituents were measured by a degenerate four-wave mixing (DF WM) technique with 7-ns pulses at 532 nm in THF and CH<sub>2</sub>Cl<sub>2</sub> solutions. The second hyperpolarizabilities ( $\gamma$ ) of these compounds widely varied in the range of 2.1 × 10<sup>-34</sup> to 2.7 × 10<sup>-32</sup> esu depending on their substituents.

Optically active, *P*-chiral phosphine– boranes were oxidized by *m*-chloroperbenzoic acid to give phosphine oxides or phosphinates with almost complete retention of configuration (shown). The oxidation of the same phosphine–boranes with iodine in the presence of water occurred with inversion of configuration in good to high stereospecificity. The reaction of the phosphine-boranes with sulfur in the presence of *N*-methylmorpholine proceeded with net retention of configration to afford optically active phosphine sulfides or phosphinothioates.

X-ray crystal structures are reported for two coordination complexes of thallium(III) chloride. In the neutral, monomeric complex [TlCl<sub>3</sub>(dmpu)<sub>2</sub>] (dmpu = N, N'-dimethylpropylene urea), the coordination geometry around the thallium centre is essentially trigonal bipyramidal with equatorial chlorines and axial dmpu ligands similar to a number of other bis-ligand complexes previously characterised. With the chelating ligand  $dppmO_2$ (Ph<sub>2</sub>P(O)CH<sub>2</sub>P(O)Ph<sub>2</sub>), the ionic compound [TlCl<sub>2</sub>(dppmO<sub>2</sub>)<sub>2</sub>] [TlCl<sub>4</sub>]·2 thf is obtained which comprises an octahedrally coordinated thallium cation with trans chlorines and a tetrahedral  $[TlCl_4]^-$  anion.





Takushi Sugino, Hiroshi Hashimoto, Yasuaki Muguruma, Nobuaki Kambe, Noboru Sonoda, Toru Sakaguchi, Masaru Miya and Koji Ohta

Substituent Effects on the Second Hyperpolarizability of Thioxanthen–9–one and Its Derivatives

325-330

T. Imamoto, K. Hirose, H. Amano and H. Seki

Stereospecific Replacement of the Boranato Group of Phosphine-Boranes by Oxygen or Sulfur. Synthesis of Optically Active, *P*-Chiral Phosphine Oxides, Phosphine Sulfides, Phosphinates, and Phos phinothioates

331-338



Claire J. Carmalt, Louis J. Farrugia and Nicholas C. Norman

Coordination Complexes of Thallium (III) Chloride

The reaction of 1,4-dimethylpiperazine with AlCl<sub>3</sub> yields the five coordinate chelate complex **1**. The unprecedented molecular structure of **1** shows it to possess an aluminum center with a trigonal bipyramidal coordination environment in which one of the axial and two of the equatorial sites are taken up by chloride ligands. Proton NMR studies on **1** are consistent with it being fluxional in solution.

Iodosylperfluoroalkanes **2** were prepared in high yield by the reaction of [bis(trifluoroacetoxy) iodo] perfluoro-alkanes **1** with sodium bicarbonate. Reactions of these compounds with 1,4-bis (trimethylsilyl) benzene in the presence of trimethylsilyltriflate gave the corresponding perfluoroalkyl (aryl) iodonium triflates **3** in 70–83% yield.

The reaction of 8-aminoquinoline with  $SbCl_3$  yields the antimony amide 1 and the antimonate salt 2 in a 1:1 ratio. Compound 1 is most likely stabilized by intramolecular donation from the aromatic nitrogen of the amido ligand, thereby forming a five-membered chelate ring. An X-ray crystal structure of 2 reveals it to possess an infinite polymeric chain consisting of chloro bridged  $[SbCl_4]^-$  units.

The conformation of the crown ether in diaquadichlorodimethyltin 15crown-5 has been verified by a low temperature X-ray diffraction study At  $-40^{\circ}$ C, crystalline (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub> 2H<sub>2</sub>O·15-crown-5,  $C_{12}H_{30}Cl_2O_7Sn_2$ exists in the monoclinic  $P2_1/c$  space group with a = 9.259(6), b = 17.072(7) $c = 13.406(4) \text{ A}, \quad \beta = 108.15(4)^{\circ}; \quad \rho =$ 1.570 g cm<sup>-3</sup>; Z = 4;  $N_{obs} = 2076$  $R_{\rm f} = 7.92\%$ . The study corrects the atom identification errors, found in the previously reported room-temperature structure, which resulted ambiguities from arising from dynamic disorder.







J. L. Atwood, C. Jones, C. L. Raston, K. D. Robinson

The First Structural Characterization of a Five Coordinate Aluminum Trichloride-Bidentate Tertiary Amine Adduct. Trichloro (1, 4-dimethylpiperazine) aluminum (III)

345-347

V. V. Zhdankin, Chris J. Kuehl, Angela J. Simonsen

Iodosylperfluoroalkanes as Reagents for the Preparation of Perfluoroalkyliodonium Salts under Aprotic Conditions

349-352

Cameron Jones, Colin L. Raston, Graham Smith

Synthesis and Characterization of Dichloro (8-quinolylamido) antimony(III) and 8-Aminoquinolinium Catena-poly[{dichloroantimonate(III)}- $\mu$ -dichloro]

353-357

Glenn P. A. Yap, Mostafa M. Amini, Seik W. Ng, Anne E. Counterman, and Arnold L. Rheingold

Thermally Induced Symmetry and Disorder: The Low-Temperature Crystal Structure of Diaquadichlorodimethyltin 15crown-5