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Index Abstracts

The interaction of antimony(III) with glycolic acid has given a complex ammonium bis[glycolato(2-)] antimony (III), which has been characterized using single-crystal X-ray diffraction methods.



G. Smith and C. H. L. Kennard

The Preparation and Crystal Structure of Ammonium Bis(glycolato) antimony (III), the First Structurally Characterised Discrete Monomeric Four-Coordinate Complex of Antimony (III) with a Dianionic α -Hydroxy Acid.

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The reaction of hexaethyldigermane with allylic halides **1** proceeded regioselectively in the presence of a catalytic amount of $Pd_2(dba)_3$ at temperatures of $120 \,^{\circ}C \sim 170 \,^{\circ}C$ giving allylgermanes **2** in 42 ~ 95% yields. The results indicate that the present reaction proceeds predominately through the S_N 2-type mechanism over an S_N 2'-type one.

T. Nakano, H. Yamashita, T. Enokido, K. Ono, and T. Migita

Palladium-Catalyzed Reactions of Hexaethyldigermane with 2-Alkenyl Halides

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$$R \xrightarrow{X} + Et_3GeGeEt_3 \xrightarrow{[Pd]} R \xrightarrow{GeEt_3} + Et_3Ge-X$$

1a: R=H, X=Br; **1b:** R=H, X=Cl; **1c:** R= 1-Ph, X=Br; **1d:** R= 1-Ph, X=Cl; **1e:** R= 1-Me, X=Br; **1f:** R=1-Me, X=Cl; **1g:** R=2-Me, X=Cl.

Reaction of elemental zinc, cadmium, or mercury with sulfur in liquid ammonia at room temperature produces X-ray amorphous metal sulfide MS (M = Zn, Cd, Hg). Thermolysis of this material at 250–300°C produced crystalline MS α -ZnS (wurtzite), α -CdS (greenockite), α -HgS (cinnabar), and β -HgS (metacinnabar). Products were characterised by microanalysis, FT-IR and Raman spectroscopy, SEM/ EDAX, X-ray powder diffraction, magnetic moment measurements, and Xray photoelectron spectroscopy.

The recently formulated second-order state-selective quasi-degenerate perturbation theory (QDPT2) is compared with quadratic configuration interaction singles and doubles (QCISD) calculations for the molecules in this study. The results of calculations using nondegenerate perturbation theory (MP2) are also reported.

Reaction of either LiPPh₂ or LiAsMes₂ with the diborane(4) compound (Me₂N)BrBBBr(NMe₂) affords the compounds (Me₂N)(Ph₂P)BB(PPh₂)(NMe₂), 1, and $(Me_2N)(Mes_2As)BB(AsMes_2)$ $(NMe_2) \cdot 0.5 PhMe$, $2 \cdot 0.5 PhMe$ (Mes = $2,4,6-Me_3C_6H_2$ -). The stereochemical activity of the phosphorus and arsenic lone pairs is demonstrated by the ready formation of the complex cis- $[Cr(CO)_4]$ $(Me_2N)(Ph_2P)BB(PPh_2)(NMe_2)] \cdot C_6H_6$ (shown), by treatment of 1 with [Cr(CO)₄(2, 5-norbornadiene)]. Compounds 1-3 were characterized by Xray crystallography, ¹¹B and ³¹P NMR spectroscopy, and by IR spectroscopy in the case of 3.

A. L. Hector, G. Henshaw, I. P. Parkin and G. A. Shaw

Room Temperature Synthesis in Liquid Ammonia of Zinc, Cadmium, and Mercury Sulfides

183-187

R. S. Winburn, B. R. Reems, M. R. Hoffmann, and C. M. Rohlfing

A Theoretical Study of the Structural Isomers of Phosphaazarine

189-196

A. Moezzi, M. M. Olmstead, D. C. Pestana, K. Ruhlandt-Senge and P. P. Power

Structural Characterization and Coordination Behavior of 1,2-Diphosphino and 1,2-Diarsino-Diborane(4) Compounds





We recently reported the neat synthesis of 3-dimensional, 6-functional cyclophosphazenic cores through a regiospecific peraminolysis of $N_3P_3Cl_6$ by long-chain diamines on suitable solid supports. Preparation of spherical dendrimers (up to the eighth generation) from such cores were achieved. Molecular modeling shows that the compactness of these dendrimers is extremely low, confer-ring to these huge monomers a noticeable vacuity for accomodation of host moieties. (A sexapus core is shown)

Herein we report that the thermolysis of acetyl-, isopropionyl-, pivaloyl-, and adamantoyltris(trimethylsilyl)silane (1-4) in the presence of 2,3-dimethyl-1,3-butadiene gives both [2 + 4] cycloadducts and ene adducts arising from the reaction of silenes generated thermally from 1-4 with butadiene, while similar reaction of benzoyland mesitoyltris(trimethylsilyl)silane (5 and 6) affords only [2 + 4] cycloadducts.

The thermolysis of 1-6 with α methylstyrene produces adducts derived from the ene reaction of the respective silenes with olefin as a single isomer. The thermolysis of 1-4 with styrene, however, affords [2 + 2] cycloadducts composed of a mixture of *cis* and *trans* isomers, while 5 and 6 produce only [2 + 2] cycloadducts with *cis* configuration. F. Sournies, F. Crasnier, C. Vidal, M.-C. Labarre and J.-F. Labarre

On the Scent of Dandelion Dendrimers. Part IV*. Molecular Modeling of Cyclophosphazenic Dandelion Dendrimers Up to the Fourth Generation

207-218



M. Ishikawa, S. Matsui, A. Naka and J. Ohshita

Silicon-Carbon Unsaturated Compounds. 53. Thermal Reactions of Acylpolysilanes

219-228

(Mc₃Si)₃SiCOR (Mc₃Si)₂Si=

R = Me, iso-Pr, tert-Bu, Ad, Ph, and Mes

A series of anhydrous calcium dithiocarbamates (DTC), and one Strontium DTC were synthesized. TGA shows the dialkyldithiocarbamates to decompose to the metal sulfide around 400°C, and the monoalkyl derivatives to start decomposing around 100°C under inert atmosphere. Two solvated calcium DTC complexes, $Ca(S_2CN(CH_2)_4)_2$ $((CH_2)_4NH)_2$ and $Ca(S_2CNH(CH_2)_3)$ NMe_2 , (THF), (H₂O) and a thiocyanate by-product were characterized by xray crystallography.

Chalcogen ring interconversion pathways have been studied by ab initio MO-techniques using suitable model reactions involving sulfur and selenium hydrides. The formation of hypervalent intermediates of types I and III seem to be energetically competetive alternatives to homolytic bond scission. The present calculations also provide an explanation why a selenium-atom transfer is preferable to a sulfur-atom transfer in the interconversion of heterocyclic selenium sulfides.

A. P. Purdy and C. F. George

Anhydrous Dithiocarbamates. Potential Precursors to Alkaline Earth Sulfide Materials

229-240



R. J. Suontamo and R. S. Laitinen

Interconversion Pathways of Chalcogen Rings An Ab Initio MO Study of Model Reactions Involving Hypervalent Sulfur and Selenium Hydrides

241-251



(1)

Excellent linear correlations between $\delta_1 = 733.8 - 15.7\sigma$ n = 10¹⁹⁹Hg shifts (δ) and Hammett substituent constants σ_m or σ_p were obtained for all three series of 37 ortho-mercurated ferrocenylimines, $(\eta^5 - C_5 H_5)$ Fe $[(\eta^5 - C_5 H_3)(HgCl)C(R) = NAr]$ (R = H (1), $CH_3(2)$, $C_6H_5(3)$; Ar = substituted phenyl groups, 1–naphthyl and 2– δ naphthyl), as shown in Equations 1, 2, and 3 for compounds 1, 2, 3, respectively.

r = -0.993

$$\delta_2 = 755.6 - 19.3\sigma$$
 $n = 10$

$$r = -0.995$$

$$\delta_3 = 761.3 - 19.9\sigma$$
 $n = 10$
 $r = -0.986$ (3)

Y. J. Wu, S. Q. Huo, H. Z. Yuan and Y. H. Liu

Secondary Interaction and $n-\pi$ Conjugation in Ferrocenylimine Deriva-(2) tives of Mercury as Probed by Hg-199 NMR

An AlCl₃-1-ethyl-3-methylimidazolium chloride (2:1) room temperature melt is studied using ¹³C and ²⁷Al relaxation methods. The Dual Spin Probe (DSP) method is used to calculate an ²⁷Al quadrupole coupling constant (χ) of 4.86 MHz which is of the same order of magnitude as values of 8.015 and 11.211 MHz obtained from *ab initio* gas phase calculations of Al₂Cl₇⁻. Linear relationships occur between ²⁷Al rotational correlation times and both viscosity (corrected for temperature) and the reciprocal of equivalent conductivity.

Poly(diphenylsilylene-co-methylene) was prepared by the Wurtz condensation:

> $x Ph_2SiCl_2 + xCH_2Br_2 + 4x Na$ $\rightarrow [Ph_2SiCH_2-]_x + 4x NaCl/Br$

The oligomeric compound was characterized and the poly(carbosilane)-toceramic conversion investigated.

 $[SiPh_2-CH_2-]_x \longrightarrow SiC_{4,8}$ The gaseous, liquid and viscous decomposition products were identified.

YbI₂(thf)₂ reacts with two equiv of KPPh₂ in tetrahydrofuran to give Yb [PPh₂]₂ (thf)₄, **1** can also be obtained from the reaction of YbI₃(thf)₃ with KPPh₂ in tetrahydrofuran in a 1:3 ratio with half an equiv of Ph₂P-PPh₂ as a byproduct as well as from Yb[N(SiMe₃)₂]₂ (thf)₂ and two equiv of Ph₂PH in tetrahydrofuran. **1** can be converted to Yb [PPh₂]₂ (N-MeIm)₄, **2**, (shown) in tetrahydrofuran using four equiv of the strong donor ligand N-methylimidazole (N-MeIm).

W. R. Carper, C. E. Keller, N. A. Evangelos and M. E. Zandler

¹³C and ²⁷Al NMR Relaxation Studies of an Acidic Chloroaluminate Melt

257-263

P. Sartori, W. Habel and T. Windmann

Pyrolysis of Poly(disphenylsilyleneco-methylene)

265-272

G. W. Rabe, J. Riede and A. Schier

Divalent Lanthanide Phosphides. Synthesis and X-Ray Crystal Structure Determination of Yb[PPh₂]₂(N-MeIm)₄: The Missing Link

273-277



The isosteric phosphonic acid analogue of tyrosine *O*-phosphate has been prepared in good yield via a three-step sequence. In addition, the nominally isosteric α -hydroxyphosphonic acid analogue of the natural phosphate has also been prepared using a direct oxidation of an intermediate in the aforementioned reaction sequence.



E. Nudelman and R. Engel

Isosteres of Natural Phosphates 12. Methylene and Hydroxymethylene Analogues of Tyrosine *O*-Phosphate

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MAIN GROUP CHEMISTRY VOLUME 1, NUMBER 2. COLOR PLATE I. See F. Sournies *et al.*, Figure 2.