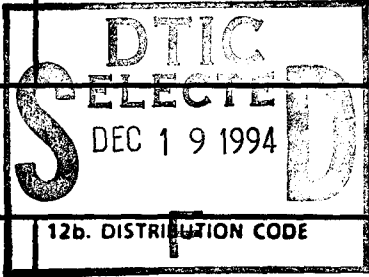


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ON THE SYNTHESIS OF MIXED-METAL AND MIXED-PNICOGEN 13-15 RING SYSTEMS

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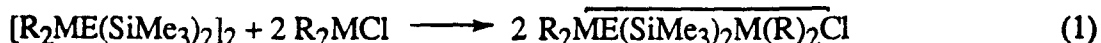
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Abstract Several pathways toward the synthesis of mixed-metal and mixed-pnicogen 13-15 ring systems have been explored. Equilibration reactions have proven successful toward the preparation of the latter compounds while most attempts to prepare mixed-metal compounds have resulted in unexpected and novel 13-15 species. These reactions and their products are discussed.

INTRODUCTION

Several compounds which have been structurally characterized by X-ray crystallography as dimeric in the solid-state have been shown to exhibit monomer-dimer equilibrium in solution.^{1,2} Based on this phenomenon, reactions involving the equilibration of two dimers, each containing different group 15 elements, were attempted.

We have reported the facile conversion of dimeric compounds, $[R_2ME(SiMe_3)_2]_2$, to their respective mixed-bridge species, $R_2\overline{ME(SiMe_3)_2M(R)_2}Cl$, by reaction with two mole equivalents of R_2MCl ($M = Ga, E = As^3$; $M = In, E = P^4$ or As^5) [eqn. 1]. In



addition, the conversion of a mixed-bridge species to its respective dimer can readily be accomplished via a salt elimination reaction using one mole equivalent of $LiE(SiMe_3)_2$ ($M = Ga, E = As^3$; $M = In, E = P^6$; $M = In, E = As^{7,8}$) [eqn. 2]. Each of these clean, high



yield reactions involved reagents which contained only the same group 13 and 15 elements and identical ligands. The success of these reactions prompted investigations into the synthesis of cyclic mixed-metal, $\overline{M-E-M'-E}$, and cyclic mixed-pnicogen, $\overline{M-E-M-E'}$, compounds.

EQUILIBRATION REACTIONSDimer Equilibrations

$[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$ (**1**) was found to exhibit monomer-dimer equilibrium at low concentrations as evidenced by the presence of both a doublet (monomer) and a triplet (dimer) in the ^1H NMR spectrum arising from the virtual coupling of the trimethylsilyl protons with phosphorus.⁷ Equimolar amounts of **1** and $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$ (**2**) were dissolved in benzene and allowed to stir for 24 h at room temperature. Removing the volatiles and recrystallizing the solid residue from cold pentane yielded crystalline $[(\text{Me}_3\text{SiCH}_2)_2\text{In}(\text{As/P})(\text{SiMe}_3)_2]_2$. An X-ray crystallographic analysis of these crystals revealed a 50:50 occupancy for As and P at the pnictogen sites. The electron ionization (20 eV) mass spectrum showed a fragmentation pattern indicative of

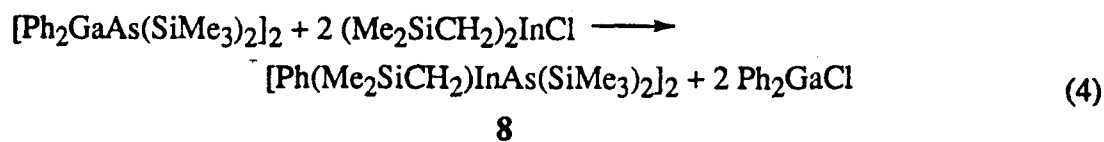
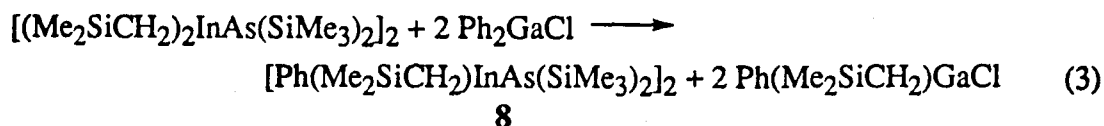
$(\text{Me}_3\text{SiCH}_2)_2\overline{\text{InAs}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{P}(\text{SiMe}_3)_2}$ (**3**) and no peaks above m/z 510 consistent with either **1** or **2**.⁹ Clusters assigned to specific ions in the mass spectrum show appropriate isotopic patterns as calculated for the atoms present.

When $[\text{I}_2\text{GaP}(\text{SiMe}_3)_2]_2$ (**4**) and $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$ (**5**), both of which exhibit monomer-dimer equilibria in solution, were combined in a 1:1 mole ratio in toluene, the crystalline compound $[\text{I}_2\text{Ga}(\text{As/P})(\text{SiMe}_3)_2]_2$ was isolated after 4 days. Like **3**, these crystals exhibited a 50:50 occupancy for As and P at the pnictogen sites. Electron ionization mass spectrometry unequivocally identified the compound as

$\text{I}_2\overline{\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{I})_2\text{P}(\text{SiMe}_3)_2}$ (**6**). Compounds **3** and **6**, both of which are extremely air sensitive, are the first examples of heavier group 13 mixed-pnictogen compounds.

Dimer and Diorganometal Halide Equilibrations

Attempts to prepare mixed-metal mixed-bridges by the equilibration of a group 13-15 dimer with a diorganometal halide [see eqn. 1] in which the halide and the dimer contained two different group 13 metals did not yield the desired compounds, but rather, unusual ligand redistribution products. The reaction of **2** with Ph_2GaCl [eqn. 3] and $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$ (**7**)¹⁰ with $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ [eqn. 4] gave the same mixed-ligand



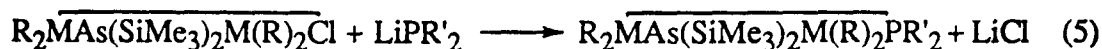
ON THE SYNTHESIS OF MIXED-METAL AND

indium-arsenic dimer $[\text{Ph}(\text{Me}_3\text{SiCH}_2)\text{InAs}(\text{SiMe}_3)_2]_2$ (**8**).¹¹ Subsequently, compound **8** was isolated in a 49.0% yield by allowing **2** to react with 2 mole equivalents of Ph_3Ga , a yield which is much higher than those of the previous two reactions (8.7% and 7.8%, respectively). Compound **8** was found to reside in the trans configuration in the solid-state, however, the ^1H NMR spectrum was consistent with the existence of equimolar amounts of the cis and trans isomers in solution at room temperature. Although it is not a mixed-metal compound, **8** was the first heavier group 13-15 compound to be fully characterized which contained two different organic substituents at the metal site. A reaction similar to that shown in eqn. 3, involving **1** and Ph_2GaCl , produced the halogen exchange product $[\text{Cl}(\text{Me}_3\text{SiCH}_2)\text{InP}(\text{SiMe}_3)_2]_2$ rather than a phenyl exchange product.¹¹

In an attempt to prevent the formation of a unique ligand exchange product, **2** was allowed to react with 2 mole equivalents of $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$ in toluene. The resulting viscous red oil was thermally unstable above -78°C . ^1H and ^{13}C NMR spectra indicated that neither of the starting materials nor the dimer $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$ were present.

SALT ELIMINATION REACTIONS

Reactions of gallium- and indium-arsenic mixed-bridging compounds with the lithium phosphides $\text{LiP}(\text{SiMe}_3)_2$ and LiPPh_2 were performed in an attempt to prepare compounds containing a four-membered ring incorporating two group 13 centers bridged by one arsenic and one phosphorus atom [eqn. 5]. When $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$ (**9**)¹⁰



and $\text{LiP}(\text{SiMe}_3)_2$ were combined in benzene at room temperature, LiCl and the unexpected ligand redistribution product $\text{Ph}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ (**10**) (29.2% yield based on arsenic) were isolated.¹² Compound **10** was later prepared in a quantitative yield by the reaction of Ph_3Ga with $\text{As}(\text{SiMe}_3)_3$.

Upon the addition of a toluene solution of **9** to a 1 mole equivalent toluene suspension of LiPPh_2 , the solid yellow phosphide appeared to react immediately. After stirring overnight at room temperature, a fine white precipitate was observed in the colorless solution. Filtering the solution separated LiCl from the liquor which, after removing the volatiles, yielded a toluene soluble white powder. ^1H NMR and a partial elemental analysis were consistent with a compound of formula

$\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{PPh}_2$ [Anal. Calcd. (Found) for $\text{C}_{42}\text{H}_{48}\text{AsGa}_2\text{PSi}_2$: C, 59.05 (58.83); H, 5.66 (5.73)]. The ^1H NMR spectrum consists of a singlet at δ 0.21

and a series of multiplets in the phenyl region, several of which appear to be further split due to virtual coupling to phosphorus. In a manner similar to that related above, the reaction of $(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ with LiPPh_2 produced LiCl and a toluene soluble powder. Elemental analysis found an As:P ratio slightly greater than 1. Several small crystals were isolated and determined crystallographically to be $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$ (**11**).¹³ The presence of this dimer would explain the deviation from unity of the As:P ratio, however, the sample consisted mainly of a powder rather than dimer **11** which readily forms large colorless crystals.

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