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

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<u>Abstract</u> 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, $R_2ME(SiMe_3)_2M(R)_2Cl$, by reaction with two mole equivalents of R_2MCl (M = Ga, E = As³; M = In, E = P⁴ or As⁵) [eqn. 1]. In

$$[R_2ME(SiMe_3)_2]_2 + 2 R_2MCl \longrightarrow 2 R_2ME(SiMe_3)_2M(R)_2Cl$$
(1)

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(SiMe₃)₂ (M = Ga, E = As³; M = In, E = P⁶; M = In, E = As^{7,8}) [eqn. 2]. Each of these clean, high

$$R_2 ME(SiMe_3)_2 M(R)_2 Cl + LiE(SiMe_3)_2 \longrightarrow [R_2 ME(SiMe_3)_2]_2 + LiCl$$
(2)

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, M-E-M'-E, and cyclic mixed-pnicogen, M-E-M-E', compounds.

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EQUILIBRATION REACTIONS

Dimer Equilibrations

[(Me₃SiCH₂)₂InP(SiMe₃)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 [(Me₃SiCH₂)₂InAs(SiMe₃)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 [(Me₃SiCH₂)₂In(As/P)(SiMe₃)₂]₂. An X-ray crystallographic analysis of these crystals revealed a 50:50 occupancy for As and P at the pnicogen sites. The electron ionization (20 eV) mass spectrum showed a fragmentation pattern indicative of

 $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ (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 $[I_2GaP(SiMe_3)_2]_2$ (4) and $[I_2GaAs(SiMe_3)_2]_2$ (5), both of which exhibit monomer-dimer equilibria in solution, were combined in a 1:1 mole ratio in toluene, the crystalline compound $[I_2Ga(As/P)(SiMe_3)_2]_2$ was isolated after 4 days. Like 3, these crystals exhibited a 50:50 occupancy for As and P at the pnicogen sites. Electron ionization mass spectrometry unequivocally identified the compound as

 $I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$ (6). Compounds 3 and 6, both of which are extremely air sensitive, are the first examples of heavier group 13 mixed-pnicogen 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 Ph₂GaCl [eqn. 3] and [Ph₂GaAs(SiMe₃)₂]₂ (7)¹⁰ with (Me₃SiCH₂)₂InCl [eqn. 4] gave the same mixed-ligand

$$[(Me_2SiCH_2)_2InAs(SiMe_3)_2]_2 + 2 Ph_2GaCl \longrightarrow [Ph(Me_2SiCH_2)InAs(SiMe_3)_2]_2 + 2 Ph(Me_2SiCH_2)GaCl (3)$$
8

$$[Ph_2GaAs(SiMe_3)_2]_2 + 2 (Me_2SiCH_2)_2InCl \longrightarrow [Ph(Me_2SiCH_2)InAs(SiMe_3)_2]_2 + 2 Ph_2GaCl$$

(4)

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indium-arsenic dimer [Ph(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (8).¹¹ Subsequently, compound 8 was isolated in a 49.0% yield by allowing 2 to react with 2 mole equivalents of Ph₃Ga, 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 Ph₂GaCl, produced the halogen exchange product [Cl(Me₃SiCH₂)InP(SiMe₃)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 $(Me_3SiCH_2)_2GaCl$ in toluene. The resulting viscous red oil was thermally unstable above -78 °C. ¹H and ¹³C NMR spectra indicated that neither of the starting materials nor the dimer [$(Me_3SiCH_2)_2GaAs(SiMe_3)_2$]₂ were present.

SALT ELIMINATION REACTIONS

Reactions of gallium- and indium-arsenic mixed-bridging compounds with the lithium phosphides LiP(SiMe₃)₂ and LiPPh₂ 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 $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (9)¹⁰

$$R_2 \overline{MAs(SiMe_3)_2 M(R)_2 Cl} + LiPR'_2 \longrightarrow R_2 \overline{MAs(SiMe_3)_2 M(R)_2 PR'_2} + LiCl \quad (5)$$

and LiP(SiMe₃)₂ were combined in benzene at room temperature, LiCl and the unexpected ligand redistribution product Ph₃Ga·As(SiMe₃)₃ (10) (29.2% yield based on arsenic) were isolated.¹² Compound 10 was later prepared in a quantitative yield by the reaction of Ph₃Ga with As(SiMe₃)₃.

Upon the addition of a toluene solution of 9 to a 1 mole equivalent toluene suspension of LiPPh₂, 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

Ph₂GaAs(SiMe₃)₂Ga(Ph)₂PPh₂ [Anal. Calcd. (Found) for C₄₂H₄₈AsGa₂PSi₂: C, 59.05 (58.83); H, 5.66 (5.73)]. The ¹H NMR spectrum consists of a singlet at δ 0.21

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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 $(Me_3SiCH_2)_2GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ with LiPPh₂ 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 $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$ (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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