Isopropylphosphido and Arsenido Derivatives of Gallium and Indium. Isolation of Gallium–Phosphorus and Indium–Phosphorus Dimers and Trimers

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Summary: The first isopropyl-substituted trimers of the type $(Me_2M(\mu\text{-E-}i\text{-Pr}_2))_3$ (**1** M = Ga, E = P; **2** M = In, E = P; **3** M = Ga, E = As) have been synthesized. The structures of **1** and **3** have been established by X-ray crystallography. The M_3E_3 rings of both compounds adopt a distorted boat conformation. On vacuum sublimation, trimers **1** and **2** are converted quantitatively into the corresponding dimers, $(Me_2Ga(\mu\text{-P-}i\text{-Pr}_2))_2$ (**4**) and $(Me_2In(\mu\text{-P-}i\text{-Pr}_2))_2$ (**5**), respectively. Preliminary OMCVD studies reveal that the mode of decomposition of **3** is significantly different from that of the analogous *t*-Bu derivatives.

Starting in 1986 there has been a rekindling of interest in compounds featuring σ bonding between the heavier group 13 and 15 elements.[1] Much of the motivation for this enhanced interest stems from the fact that some of these compounds can function as single source precursors to compound semiconductors such as gallium arsenide and indium phosphide. The 1:1 stoichiometry compounds of empirical formula $R_2MER'_2$ have been found to adopt monomeric, dimeric, or trimeric structures. If the substituents on M and/or E are of modest size, trimers are isolated while sterically demanding substituents promote monomer or dimer formation.[1] For the molecules $[(Me_3SiCH_2)_2AsGa(Cl)R]_{2,3}$ (R = Me, Ph) the steric situation is such that dimer/trimer equilibrium in solution is detectable spectroscopically.[2] We report the first example of the isolation of dimers and trimers of the same empirical composition, viz. $[Me_2M(\mu\text{-P-}i\text{-Pr}_2)]_2$ and $[Me_2M(\mu\text{-P-}i\text{-Pr}_2)]_3$ (M = Ga, In). These compounds also represent the first examples of isopropyl-substituted $(ME)_2$ or $(ME)_3$ rings. Previous experience has shown that the presence of β-hydrogen atoms is desirable for facilitating hydrocarbon elimination at relatively modest temperatures.[3]

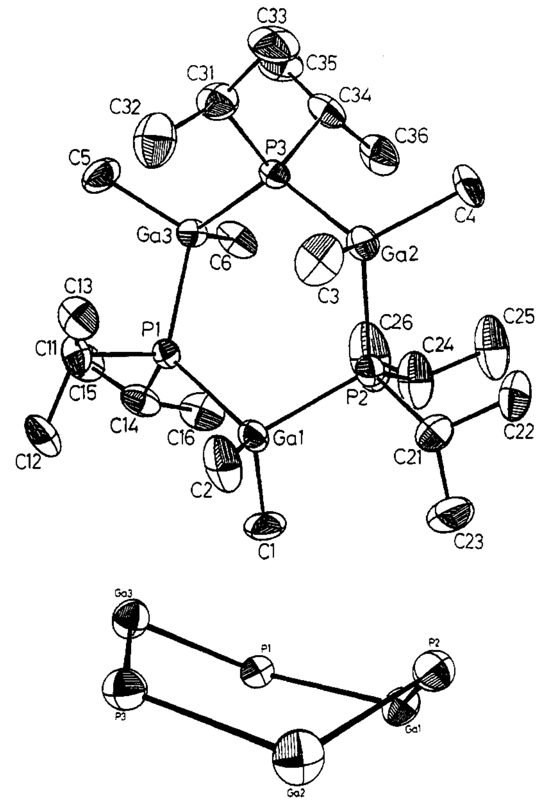

Figure 1. ORTEP view of 1 showing the atom numbering scheme (above) and the conformation of the Ga_3P_3 ring (below). Important bond distances (Å) and angles (deg) are given in Table I.

Table I. Key Bond Lengths (Å) and Angles (deg) for 1[a]

Bond Distances			
Ga1–P1	2.442 (3)	Ga2–C3	2.01 (1)
Ga1–P2	2.428 (3)	Ga2–C4	2.01 (1)
Ga1–C1	2.02 (1)	Ga3–P1	2.457 (3)
Ga1–C2	2.02 (1)	Ga3–P3	2.438 (3)
Ga2–P2	2.419 (3)	Ga3–C5	2.01 (1)
Ga2–P3	2.431 (3)	Ga3–C6	2.02 (1)
Bond Angles			
P1–Ga1–P2	108.1 (1)	Ga1–P1–Ga3	124.5 (1)
P1–Ga1–C1	109.1 (5)	Ga1–P1–C11	104.6 (4)
P1–Ga1–C2	112.2 (5)	Ga1–P1–C14	107.0 (4)
P2–Ga1–C1	111.2 (3)	Ga3–P1–C11	108.8 (4)
P2–Ga1–C2	104.1 (3)	Ga3–P1–C14	107.6 (4)
C1–Ga1–C2	112.0 (6)	C11–P1–C14	102.2 (6)
P2–Ga2–P3	108.4 (1)	Ga1–P2–Ga2	114.1 (1)
P2–Ga2–C3	102.2 (4)	Ga1–P2–C21	101.7 (4)
P2–Ga2–C4	114.4 (4)	Ga1–P2–C24	109.8 (5)
P3–Ga2–C3	110.0 (4)	Ga2–P2–C21	104.1 (4)
P3–Ga2–C4	108.0 (4)	Ga2–P2–C24	118.9 (5)
C3–Ga2–C4	113.6 (6)	C21–P2–C24	106.3 (6)
P1–Ga3–P3	107.9 (1)	Ga2–P3–Ga3	123.6 (1)
P1–Ga3–C5	110.6 (4)	Ga2–P3–C31	107.9 (4)
P1–Ga3–C6	109.4 (4)	Ga2–P3–C34	107.6 (4)
P3–Ga3–C5	109.2 (4)	Ga3–P3–C31	107.3 (4)
P3–Ga3–C6	109.2 (4)	Ga3–P3–C34	107.9 (4)
C5–Ga3–C6	110.5 (5)	C31–P3–C34	100.0 (5)

Treatment of $i\text{-Pr}_2PLi$ with 1 equiv of $GaCl_3$ and 2 equiv of MeLi resulted in the trimer $[Me_2Ga(\mu\text{-P-}i\text{-Pr}_2)]_3$ (1) (Figure 1). The corresponding indium compound $[Me_2In(\mu\text{-P-}i\text{-Pr}_2)]_3$ (2) was prepared via the reaction of $i\text{-Pr}_2PLi$ with Me_2InCl. The analogous gallium–arsenic trimer $[Me_2Ga(\mu\text{-As-}i\text{-Pr}_2)]_3$ (3) resulted from the thermal reaction of Me_3Ga with $i\text{-Pr}_2AsH$. Compounds 1–3 were characterized spectroscopically and 1 and 3 were also investigated by X-ray crystallography. Key bond lengths and angles for 1 and 3 are given in Tables I and II, respectively. It has been noted previously that six-membered M_3E_3 rings exhibit conformational flexibility.[1] A distorted boat conformation is adopted by both 1 and 3 and there are no short intermolecular contacts.[4] The average Ga–P (2.436 (3) Å) and Ga–As (2.517 (2) Å) bond lengths in 1 and 3 are somewhat longer than the sums of the Ga–P (2.36 Å) and Ga–As (2.44 Å) Pauling single bond covalent radii.[5]

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[4] Deviations (Å) from the best least squares plane for 1: Ga(1), −0.058 (1); Ga(2), 0.058 (1); Ga(3), −0.548 (1); P(1), 0.059 (3); P(2), −1.040 (3); P(3), −0.060 (3). For 3: Ga(1), 0.058 (1); Ga(2), 0.059 (1); Ga(3), −0.526 (1); As(1), 0.062 (1); As(2), −1.065 (1); As (3), −0.062 (1).

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Table II. Key Bond Lengths (Å) and Angles (deg) for 3[a]

	Bond Distances		
As1–Ga1	2.529 (2)	As3–Ga3	2.527 (2)
As1–Ga3	2.531 (2)	As3–C31	2.02 (1)
As1–C11	2.00 (1)	As3–C34	2.01 (1)
As1–C14	2.01 (1)	Ga1–C1	2.01 (1)
As2–Ga1	2.505 (2)	Ga1–C2	2.00 (1)
As2–Ga2	2.498 (2)	Ga2–C3	2.01 (1)
As2–C21	2.03 (1)	Ga2–C4	2.02 (1)
As2–C24	1.99 (1)	Ga3–C5	2.00 (1)
As3–Ga2	2.513 (2)	Ga3–C6	2.02 (1)
	Bond Angles		
Ga1–As1–Ga3	127.52 (6)	As1–Ga1–As2	105.14 (6)
Ga1–As1–C11	106.2 (4)	As1–Ga1–C1	109.3 (4)
Ga1–As1–C14	107.3 (4)	As1–Ga1–C2	112.7 (4)
Ga3–As1–C11	107.4 (4)	As2–Ga1–C1	111.1 (4)
Ga3–As1–C14	106.1 (4)	As2–Ga1–C2	104.0 (4)
C11–As1–C14	98.7 (5)	C1–Ga1–C2	114.2 (6)
Ga1–As2–Ga2	116.56 (5)	As2–Ga2–As3	106.06 (6)
Ga1–As2–C21	101.1 (4)	As2–Ga2–C3	100.9 (4)
Ga1–As2–C24	108.9 (4)	As2–Ga2–C4	114.4 (4)
Ga2–As2–C21	103.3 (4)	As3–Ga2–C3	109.6 (4)
Ga2–As2–C24	119.4 (4)	As3–Ga2–C4	108.7 (4)
C21–As2–C24	105.0 (5)	C3–Ga2–C4	116.5 (6)
Ga2–As3–Ga3	125.82 (6)	As1–Ga3–As3	105.92 (5)
Ga2–As3–C31	106.5 (4)	As1–Ga3–C5	108.8 (4)
Ga2–As3–C34	106.9 (4)	As1–Ga3–C6	109.0 (4)
Ga3–As3–C31	108.2 (3)	As3–Ga3–C5	109.6 (4)
Ga3–As3–C34	107.8 (4)	As3–Ga3–C6	109.0 (3)
C31–As3–C34	98.2 (5)	C5–Ga3–C6	114.2 (5)

Vacuum sublimation of 1 (150 °C, 10^{-2} Torr) and 2 (110 °C, 10^{-2} Torr) resulted in the isolation of the corresponding dimers $[Me_2Ga(\mu\text{-}P\text{-}i\text{-}Pr_2)]_2$ (4) and $[Me_2In(\mu\text{-}P\text{-}i\text{-}Pr_2)]_2$ (5), respectively. Neither of these colorless solids was suitable for single-crystal X-ray analysis. However, the dimeric nature of 4 and 5 was established definitively by the presence of parent peaks in the mass spectra. The ^{31}P NMR spectral parameters of 1, 2, 4, and 5 enable one to differentiate between the presence of dimers and trimers in solution. Thus, solutions of the trimers 1 and 2 give $^{31}P\{^1H\}$ NMR chemical shifts of δ −41.0 and −36.3, respectively. These are the thermodynamically most stable species, and there is no evidence of the dimers 4 and 5. Fresh solutions of the dimers 4 and 5 show sharp singlets at δ −11.0 and −2.1, respectively. However, there are significant differences in the stabilities of dimers 4 and 5 in solution. Thus, in C_6H_6 solution, the indium–phosphorus dimer 5, reverts to the corresponding trimer, 2, in a few minutes at 25 °C while the analogous gallium–phosphorus dimer, 4, persists for over one week under the same conditions. Presumably, this stability difference relates to the metal–phosphorus bond strengths. In addition, it is interesting to note that all of the Ga–As bond lengths in 3 [range 2.498 (2)–2.513 (2) Å] are longer than any of those found in $[(Me_3SiCH_2)_2AsGaBr_2]_3$ [range 2.432 (2)–2.464 (1) Å]. For the latter, the $(Ga–As)_3$ ring has a twist-boat conformation and the average Ga–As bond length of 2.450 (2) Å is very close to the sum of single-bond covalent radii (2.44 Å).[6] As noted earlier,[1] the M–E bond lengths of $(ME)_n$ rings are sensitive to the steric and electronic characteristics of the ligands.

An OMCVD study of $[Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)]_2$ revealed that at 570 °C methane and isobutene are the predominant hydrocarbons evolved during GaAs film growth, thus suggesting a β-hydrogen shift mechanism.[3] In the case of 3, competing mechanisms appear to be operative since the volatile products include both C_4 and C_6 hydrocarbons. Further studies are in progress.

Experimental Section

All compounds were prepared under dry nitrogen with use of standard vacuum-line techniques. Toluene was distilled from sodium metal under nitrogen before use. Hexane and THF were distilled from sodium benzophenone ketyl under nitrogen. The compounds $i\text{-}Pr_2AsH$ and $i\text{-}Pr_2PH$ were prepared by methods similar to those described previously.[7] Instruments: IR, Perkin-Elmer 1330; NMR (^1H and ^{31}P), GE 300. IR spectra were recorded as KBr disks. NMR spectra were recorded in C_6D_6 at ambient temperature and are referenced to Me_4Si (δ 0.0, ^1H) and 85% H_3PO_4 (aqueous) (δ 0.0, ^{31}P).

Synthesis of 1. $i\text{-}Pr_2PLi$ was prepared by adding 4 mL of 1.8 M *n*-BuLi solution to 0.83 g (7.1 mmol) of $i\text{-}Pr_2PH$ in 30 mL of THF at −78 °C. After slow warming to room temperature, the stirred mixture was recooled to −78 °C and treated simultaneously with a solution of 1.25 g (7.1 mmol) of $GaCl_3$ in 20 mL of THF and 9.1 mL of a 1.56 M solution of MeLi in Et_2O (14.2 mmol). The reaction mixture was allowed to assume ambient temperature and was stirred overnight, following which the solvent and volatiles were removed under vacuum. The resulting residue was extracted with toluene, filtered, concentrated, and cooled to −50 °C. Colorless crystals of 1 (mp 166–7 °C) were produced in 63% yield.

Synthesis of 2. A solution of 11.0 mmol of $i\text{-}Pr_2PLi$ in 20 mL of THF (vide supra) was added dropwise to a solution of Me_2InCl (1.97 g, 11.0 mmol) in 30 mL of THF at −78 °C. The rest of the procedure was essentially the same as that described above for 1. Colorless microcrystalline 2 (mp 172–173 °C) was produced in 82% yield.

Synthesis of 3. A mixture of $i\text{-}Pr_2AsH$ (0.3 g, 1.85 mmol) and Me_3Ga (0.21 g, 1.85 mmol) was heated at 130 °C until a white solid was formed. Methylene chloride (5 mL) was added to the reaction mixture; colorless crystals of 3 (mp 204–5 °C) formed upon cooling the resulting solution to −20 °C.

Conversion of 1 and 2 into 4 and 5. This was accomplished by vacuum sublimation of 1 (110 °C, 10^{-2} Torr) and 2 (150 °C, 10^{-2} Torr). Monitoring of these sublimations by ^{31}P NMR indicated that the conversions are quantitative. The mp's of 4 and 5 are 147–9 and 159–60 °C, respectively.

Spectroscopic Data. $^{31}P\{^1H\}$ NMR (121.5 MHz, 295 K, 85% H_3PO_4 external standard): δ 1 (C_6D_6), −41.0; 2 (C_6D_6), −36.3; 4 (C_6D_6), −11.0; 5 (C_6D_6), −2.1. ^1H NMR (300.15 MHz, 295 K, C_6D_6): δ 1, 2.2 (6 H, m, J = 7 Hz, $HC(CH_3)_2$) 1.2 (36 H, q, J = 7 Hz, $(CH_3)_2C$), 0.1 (18 H, m, CH_3Ga); 2, 2.2 (6 H, septet, J = 6.9 Hz, $HC(CH_3)_2$), 1.2 (36 H, q, J = 6.9 Hz, $(CH_3)_2C$), 0.1 (18 H, s, CH_3In); 3, 2.4 (6 H, septet, J = 7.2 Hz, $HC(CH_3)_2$), 1.3 (36 H, d, J = 7.2 Hz, $(CH_3)_2C$), 0.3 (18 H, s, CH_3Ga); 4, 2.1 (6 H, m, J = 6.9 Hz, $HC(CH_3)_2$), 1.1 (24 H, q, J = 6.9 Hz, $(CH_3)_2C$), 0.1 (12 H, t, J = 3.9 Hz, CH_3Ga); 5, 2.1 (4 H, m, J = 6.9 Hz, $HC(CH_3)_2$), 1.1 (24 H, q, J = 6.9 Hz, $(CH_3)_2C$), 0.2 (12 H, t, J = 2.4 Hz, CH_3In).

MS: 1 (CI, CH_4), 636 ($M^+ - CH_3$), 534 (M^+ − P-*i*-Pr_2); 2 (CI, CH_4), 786 (M^+), 771 ($M^+ - CH_3$), 741 ($M^+ - 2CH_3$); 3 (CI, CH_4), 768 ($M^+ - CH_3$), 683 ($M^+ - GaMe_2$), 653 ($M^+ - GaMe_2 - 2Me$); 4 (CI, CH_4), 434 (M^+), 419 ($M^+ - CH_3$), 317 (M^+ − P-*i*-Pr_2); 5 (EI, 70 eV), 524 (M^+), 509 ($M^+ - CH_3$), 407 (M^+ − P-*i*-Pr_2). Anal. Calcd for $C_{24}H_{60}Ga_3P_3$ (1): C, 44.29; H, 9.29. Found: C, 44.03; H, 9.21. Calcd for $C_{24}H_{60}In_3P_3$ (2): C, 36.67; H, 7.69. Found: C, 36.85; H, 7.53. Calcd for $C_{24}H_{60}Ga_3As_3$ (3): C, 36.83; H, 7.73. Found: C, 36.58; H, 7.55. Calcd for $C_{16}H_{40}Ga_2P_2$ (4): C, 44.29; H, 9.29. Found: C, 44.11; H, 9.15. Calcd for $C_{16}H_{40}In_2P_2$ (5): C, 36.67; H, 7.69. Found: C, 36.55; H, 7.50.

X-ray Experimental Details for 1 and 3. Crystals of 1 and 3 were sealed in thin-walled glass capillaries under nitrogen. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 1 °C by using graphite monochromated Mo K_α radiation. All calculations were performed on a Microvax-II computer with the Enraf-Nonius software package SDP-PLUS.[8] For each structure

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the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MULTAN)[9] or Patterson methods, and successive cycles of difference Fourier maps followed by least-squares refinement. Scattering factors were taken from ref 10.

1: Monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$; $a = 15.910$ (4), $b = 10.294$ (6), $c = 20.817$ (7) Å; $\beta = 98.63$ (2)°; $V = 3371$ Å^3; d(calcd) = 1.282 g cm^{-3}; 3° < 2θ < 55° (Mo K$_\alpha$, $\lambda = 0.71069$ Å; $\mu = 25.2$ cm^{-1}). 2: Monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$; $a = 16.118$ (7), $b = 10.398$ (2), $c = 20.996$ (4) Å; $\beta = 98.87$ (3)°; $V = 3477$ Å^3; d(calcd) = 1.495 g cm^{-3}; 3° < 2θ < 50° (Mo K$_\alpha$, $\lambda = 0.71069$ Å; $\mu = 51.4$ cm^{-1}). Totals of 5919 and 6108 unique reflections were collected at 24 °C for 1 and 3, respectively. Of these, 3035 and 3414 reflections with $I > 3.0\sigma(I)$ were used to solve (direct methods) and refine (full-matrix, least squares) the structures of 1 and 3, respectively. The final R and R_w values were 0.053 and 0.061 for 1 and 0.042 and 0.050 for 3. C13 in the structure of 1 is disordered. There is a 50:50 occupancy of positions C13A and C13B.

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Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for 1 and 3 (13 pages); listings of structure factor amplitudes for 1 and 3 (33 pages). Ordering information is given on any current masthead page.

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Reactivity of Early-Transition-Metal Fulvene Complexes. Transformation of a 2,3,4,5-Tetramethylfulvene Ligand into a Bidentate Dialkoxide with Four Asymmetric Carbon Atoms. Molecular Structure of $Ti[(OCHPh)_2C_5Me_4(CH_2)]Cl_2$

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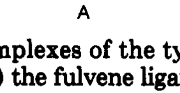
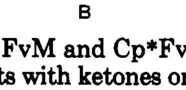
Summary: Cp*FvTiCl (**1**; Cp* = η^5-C_5H_5, Fv = η^6-$C_5Me_4CH_2$) reacts with benzaldehyde, yielding Cp*Ti-$[(OCHPh)_2C_5Me_4(CH_2)]Cl$ (**2**) as the result of insertion in two Ti–C bonds at the 2- and 4-positions of the fulvene ligand in **1**. Complex **2** reacts with HCl to give Cp*$TiCl_3$ (**3**) and the corresponding dialcohol and with $TiCl_4$ to give **3** and $Ti[(OCHPh)_2C_5Me_4(CH_2)]Cl_2$ (**5**). X-ray diffraction analysis of **5** shows it to be a dialkoxide–dichloride monomeric titanium complex with a tetrahedral arrangement of the ligands around the metal center. Crystal data for $C_{24}H_{26}Cl_2O_2Ti$: monoclinic, $P2_1/n$, $a = 10.602$ (5) Å, $b = 14.157$ (4) Å, $c = 15.274$ (5) Å, $\beta = 103.76$ (3)°, $V = 2227$ (1) Å^3, $Z = 4$, $R = 0.037$.

The bonding of a tetramethylfulvene ligand to early transition metals has been described as intermediate between the two extremes A and B.[1]



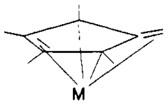
A



B

In complexes of the type Cp*FvM and Cp*FvMCl (M = Ti, Zr) the fulvene ligand reacts with ketones or nitriles, through an adduct intermediate, to give bidentate alkoxide- or amide-functionalized tetramethylcyclopentadienyl groups.[2] This reactivity can be explained in terms of the cyclopentadienyl alkyl structure A. Nevertheless, spectroscopic and structural data for these compounds point to a significant contribution of structure B.[3] A different bonding of the fulvene group is observed in late-transition-metal fulvene complexes, where in some cases the ligand appears to be bonded as a η^4-diene[4] or η^2-olefin[5] and extrusion of the fulvene ligand is observed.[6]

We wish to report here an unprecedented reactivity of this type of ligand that can be well understood in terms of another bonding form, C, a special type of 1,3-diene complex, in which the diene coordinates in a σ^2,π mode as has been observed for a number of Zr and Hf complexes.[7]



C

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