

Dimeric Gallium and Indium Dialkylphosphido Complexes with Unusual Group 13-15 Stoichiometries

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Three group 13 dialkylphosphido complexes have been prepared with group 13-15 stoichiometries of 1:2, [*t*-Bu(*i*-Pr₂P)Ga(μ -P-*i*-Pr₂)₂] (1) and [*i*-Pr(*i*-Pr₂P)In(μ -P-*i*-Pr₂)₂] (2), and 2:3, [*t*-Bu(*i*-Pr₂P)Ga(μ -P-*i*-Pr₂)₂Ga(Cl)*t*-Bu] (3). These complexes were prepared in moderate yields via the reaction of the appropriate lithium dialkylphosphide and alkyl group 13 halide in the desired stoichiometric ratio. Each compound has been characterized by elemental analysis, ¹H and ³¹P NMR, and mass spectroscopy. The structures of 2 and 3 were established by X-ray crystallography. Crystal data for 2: space group *P*2₁/*c*, *a* = 11.283(1) Å, *b* = 11.429(5) Å, *c* = 15.836(3) Å, β = 104.19(1)°, *V* = 1980(6) Å³, *Z* = 4, *R* = 0.0401. Crystal data for 3: space group *P*2₁/*c*, *a* = 18.453(4) Å, *b* = 9.516(2) Å, *c* = 20.745(4) Å, β = 106.88(3)°, *V* = 3486(2) Å³, *Z* = 8, *R* = 0.0551. Both compounds feature structures with four-membered M₂P₂ rings.

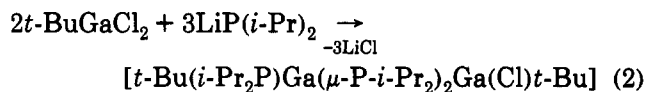
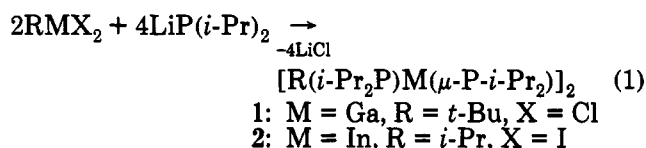
Introduction

Molecules with group 13-15 bonding have been used widely in the single-source precursor approach to thin films of semiconducting materials.¹ Initial attention was focused on molecules possessing group 13:15 (M-E) mole ratios of 1:1 because this matches the stoichiometry of the desired solid-state material (ME).² However, deposition studies with these 1:1 precursors revealed that the resulting films are p-type due to a deficiency of the group 15 element. More recently, therefore, attention has shifted to precursors of general formula [M(ER₂)₃]_{*n*} which, having a 1:3 stoichiometry, feature an excess of the group 15 element on the surface during film growth.³ Although homoleptic 13-15 combinations of this type are well-represented in the literature,⁴ molecules with intermediate stoichiometries such as 1:2, and 2:3 are rare, and in fact limited to the dimeric 1:2 complexes [ClIn(μ -Sb-*t*-Bu₂)₂]₂⁵ and [ClGa(μ -NMe₂)₂]₂.⁶ As part of our continuing interest in single-

source precursor molecules to 13/15 materials, we have prepared and characterized two new examples of 1:2 complexes, [*t*-Bu(*i*-Pr₂P)Ga(μ -P-*i*-Pr₂)₂] (1) and [*i*-Pr(*i*-Pr₂P)In(μ -P-*i*-Pr₂)₂] (2), and the first example of a 2:3 complex, [*t*-Bu(*i*-Pr₂P)Ga(μ -P-*i*-Pr₂)₂Ga(Cl)*t*-Bu] (3).

Results and Discussion

Synthesis of Compounds 1-3. Compounds 1 and 2 were synthesized in moderate yield (63-68%) via the salt elimination reaction of the appropriate alkyl-substituted metal dichloride with 2 equiv of LiP(*i*-Pr)₂ in Et₂O or THF at -78 °C (eq 1). Compound 3 was also prepared by salt



elimination methodology (eq 2). Compound 3 can be converted into 1 in virtually quantitative yield by treatment with 1 equiv of LiP(*i*-Pr)₂ in THF or Et₂O solution at 25 °C. Compounds 1-3 can also be prepared, but in lower yields, via the reaction of in situ generated group 13 phosphide halides of the general type Cl_{3-*n*}M(P-*i*-Pr₂)_{*n*} (M = Ga, In; *n* = 1, 2) with the appropriate alkyllithium reagent. Unsuccessful attempts were made to isolate the phosphide halide intermediates.

Spectroscopic Characterization of Compounds 1-3. Mass spectral data for 1-3 (Experimental Section) are

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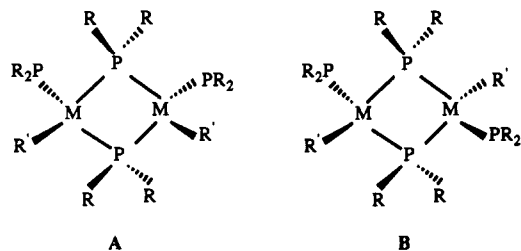
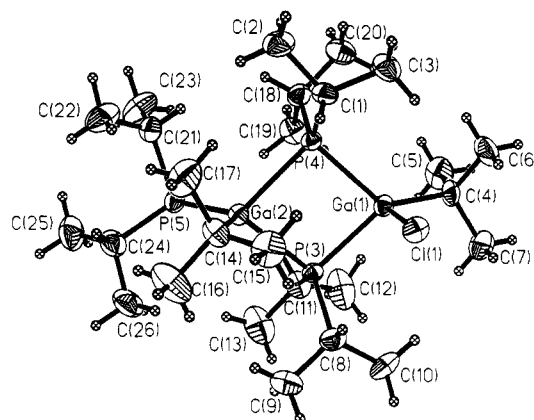
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Table I. ^{31}P Chemical Shifts for Selected Group 13 Phosphido Compounds

compd	δ (ppm)	ref
$[t\text{-Bu}(i\text{-Pr}_2\text{P})\text{Ga}(\mu\text{-P-}i\text{-Pr}_2)]_2$ (1)	22.07 (b), 13.04 (t) ^a	
$[\text{Me}_2\text{Ga}(\mu\text{-P-}t\text{-Bu})_2]_2$	28.41	7
$[n\text{-Bu}_2\text{Ga}(\mu\text{-P-}t\text{-Bu})_2]_2$	32.9	7
$[t\text{-Bu}_2\text{Ga}(\mu\text{-P(H)C}_5\text{H}_9)]_2$	-90.3, -94.5 ^b	8
$[(\text{Me}_3\text{SiCH}_2)_2\text{Ga}(\mu\text{-PPh}_2)]_2$	-40.25	9
$\text{Ga}(\text{P-}t\text{-Bu}_2)_3$	34.80	7
$[n\text{-Bu}_2\text{In}(\mu\text{-P-}t\text{-Bu})_2]_2$ ^c	46.66	
$[i\text{-Pr}(i\text{-Pr}_2\text{P})\text{In}(\mu\text{-P-}i\text{-Pr}_2)]_2$ (2)	12.80 (b), 3.66 (t)	
$[(\text{Me}_3\text{SiCH}_2)_2\text{In}(\mu\text{-PPh}_2)]_2$	-50.30	9
$\text{In}(\text{P-}t\text{-Bu}_2)_3$	70.80	1
$[t\text{-Bu}(i\text{-Pr}_2\text{P})\text{Ga}(\mu\text{-P-}i\text{-Pr}_2)_2\text{Ga}(\text{Cl})t\text{-Bu}]$ (3)	14.81 (b), -20.60 (t)	

^a t = terminal; b = bridge. ^b Cis and trans isomers present. ^c This compound was prepared in 66% yield from $n\text{-Bu}_2\text{InCl}$ and $\text{LiP-}t\text{-Bu}_2$ in a similar fashion to that described for 1 and 2. Anal. Calcd for $\text{C}_{28}\text{H}_{63}\text{In}_2\text{P}_2$: C, 51.35; H, 9.70. Found: C, 50.97; H, 9.94. Mp: 80–81 °C.

indicative of dimeric formulations for all three compounds. This indication was supported by the observation of two ^{31}P NMR (singlet) resonances for each compound (Table I). Although the assignments for bridging and terminal phosphido groups for 1–3 should not be regarded as unequivocal, the proposed assignments are consistent with (i) the observation that the homoleptic species, $\text{M}(\text{P-}t\text{-Bu}_2)_3$ ($\text{M} = \text{Ga}, \text{In}$), which feature only terminal PR_2 moieties, exhibit more positive ^{31}P chemical shifts than compounds with bridging phosphido entities, and (ii) the general trends in ^{31}P chemical shifts versus phosphorus coordination number. It should also be noted that there are two possible isomers for 1 and 2, namely cis (A) and

**Figure 1.****Figure 2.**

trans (B) with respect to the disposition of the $t\text{-Bu}$ or $i\text{-Pr}$ groups. Both isomers would exhibit two ^{31}P signals; hence it was necessary to undertake an X-ray analysis of 1 and/or 2 to provide unambiguous structural characterization. Matters are somewhat more complicated in the case of 3 because of the further dichotomy of bridging chloride and bridging phosphido isomers. Again, X-ray crystallography was necessary to establish the isomeric preference in the solid state.

X-ray Crystal Structures of $[i\text{-Pr}(i\text{-Pr}_2\text{P})\text{In}(\mu\text{-P-}i\text{-Pr}_2)]_2$ (2) and $[t\text{-Bu}(i\text{-Pr}_2\text{P})\text{Ga}(\mu\text{-P-}i\text{-Pr}_2)_2\text{Ga}(\text{Cl})t\text{-Bu}]$ (3). Compound 2 crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. There are no unusually short intermolecular contacts and individual molecules of 2 reside on an inversion center. The molecular structure and atom numbering scheme are shown in Figure 1, and selected bond distances and angles are presented in Table II. The dimeric molecules of 2 are held together by phosphido bridges, and the $i\text{-Pr}$ and terminal phosphido moieties adopt a mutually trans arrangement (isomer B). As a further consequence of the presence of an inversion center, the In_2P_2 core of 2 is planar. However, the pattern of bond angles within the In_2P_2 rhombus is unusual. The normal pattern of bond angles in M_2E_2 systems is such that the M-E-M angles exceed

the E-M-E angles.¹ However, in 2 this pattern is reversed with $\text{P-In-P} = 107.3(8)^\circ$ and $\text{In-P-In} = 72.6(1)^\circ$. The obtuse P-In-P angle results in an $\text{In}\cdots\text{In}$ separation of 4.018(1) Å. Interestingly, this distance is only slightly longer than the $\text{In}\cdots\text{In}$ separations in the $\text{In}(1)$ compounds $[\text{In}(\text{C}_5\text{Me}_5)]_6$ (3.952(1) Å)¹¹ and $[\text{In}(\text{C}_5\text{H}_5)]_\infty$ (3.986(1) Å).¹² The endocyclic In-P bond distance in 2 (2.642(1) Å) is similar to those found in $[(\text{Me}_3\text{SiCH}_2)_2\text{In}(\mu\text{-PPh}_2)]_2$ (2.649(2) Å)⁹ and $[\text{Et}_2\text{In}(\mu\text{-P-}t\text{-Bu})_2]$ (2.635(2) Å).¹⁰ The exocyclic In-P bond distance in 2 (2.574(1) Å) is shorter than the endocyclic distance and close to that in the homoleptic compound, $\text{In}(\text{P-}t\text{-Bu}_2)_3$ (2.591(14) Å).¹⁰ Such a trend in endo- and exocyclic bond distances has been noted previously in, e.g., $[(t\text{-Bu}_2\text{Sb})(\text{Cl})\text{In}(\mu\text{-Sb-}t\text{-Bu}_2)]_2$.⁵

Crystals of 3 belong to the monoclinic space group $P2_1/c$. There are four molecules in the unit cell, and there are no unduly short intermolecular contacts. The molecular structure is illustrated in Figure 2 along with the atom numbering scheme. A selection of bond distances and angles is presented in Table II. Individual molecules of 3 are dimeric and feature two bridging $i\text{-Pr}_2\text{P}$ groups; the remaining $i\text{-Pr}_2\text{P}$ group, two $t\text{-Bu}$ groups, and a chloride ligand therefore occupy the four terminal positions. As

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Table II. Selected Bond Distances (Å) and Angles (deg) for Group 13 Phosphido Compounds

compd	M-P (bridging)	M-P (terminal)	M-P-M'	P-M-P'	ref
[Me ₂ Ga(μ-P- <i>t</i> -Bu) ₂] ₂	2.474(5)			93.5(1)	7
[<i>n</i> -Bu ₂ Ga(μ-P- <i>t</i> -Bu) ₂] ₂	2.476(5)			93.3(2)	7
[<i>t</i> -Bu ₂ Ga(μ-P(H)C ₃ H ₉) ₂] ₂	2.451(1)			98.24(3)	8
[<i>i</i> -Pr(<i>i</i> -Pr ₂ P)In(μ-P- <i>i</i> -Pr ₂) ₂] ₂ (2)	2.642(1)	2.574(1)		72.6(1)	107.3(8)
[(Me ₃ SiCH ₂) ₂ In(μ-PPh ₂) ₂] ₂	2.649(2)			97.48(8)	82.51(7)
[<i>t</i> -BuGa(P- <i>i</i> -Pr ₂)(μ-P- <i>i</i> -Pr ₂) ₂ ClGa(<i>t</i> -Bu)] (3)	2.486(2), 2.501(2)	2.391(2)		93.4(1)	83.5(1)
	2.411(2), 2.410(2)			93.1(1)	87.0(1)
[Et ₂ In(μ-P- <i>t</i> -Bu) ₂] ₂	2.635(2)			94.4(1)	85.6(1)
In(P- <i>t</i> -Bu) ₃	2.591(14)				10

Table III. Crystal Data, Details of Intensity Measurement, and Structural Refinement for [*i*-Pr(*i*-Pr₂P)In(μ-P-*i*-Pr₂)₂]₂ (2) and [*t*-Bu(*i*-Pr₂P)Ga(μ-P-*i*-Pr₂)₂Ga(Cl)*t*-Bu] (3)

compd	2	3
formula	C ₃₀ H ₇₀ In ₂ P ₄	C ₂₆ H ₆₀ Cl ₁ Ga ₂ P ₃
fw	784.42	640.58
cryst dimen, (mm)	0.5 × 0.4 × 0.8	0.4 × 0.4 × 0.3
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /c
a, Å	11.283(1)	18.453(2)
b, Å	11.429(5)	9.516(2)
c, Å	15.836(3)	20.745(4)
α, deg	90	90
β, deg	104.19(1)	106.88(3)
γ, deg	90	90
V, Å ³	1980(6)	3486(2)
D(calc), g cm ⁻³	1.325	1.21
Z	8	4
radiation	Mo Kα	Mo Kα
no. of total reflns	3246	5727
no. of obsd reflns	2718	3191
sig test	I > 5σ(I)	I > 4σ(I)
no. of param	163	289
weighting scheme g in [(σF) ² + gF ²] ⁻¹	0.000 325	0.0008
final R	0.0401	0.0511
final R _w	0.0509	0.0547

in the case of 2, the two alkyl groups adopt a mutually trans disposition. As expected on the basis of the different patterns of substitution at Ga(1) and Ga(2), the endocyclic P-Ga-P angles are different at these two centers (P(3)-Ga(1)-P(4) = 87.0(1)°, P(3)-Ga(2)-P(4) = 83.5(1)°, and P(3)-Ga(2)-P(4) = 83.4(1)°). The wider angle at Ga(1) presumably results from the replacement of an *i*-Pr₂P group by a less sterically demanding chloride ligand. Such a view gains support from the fact that the P(5)-Ga(2)-C(14) angle is 123.2(2)° while that of Cl-Ga(1)-C(4) is 104.7(3)°. As expected, the endocyclic angles at P(3) and P(4) are identical within experimental error. Note also that the sum of endocyclic bond angles is 357.0°, thus indicating a slight nonplanarity of the Ga₂P₂ ring. The presence of bulkier substituents on Ga(2) also causes the endocyclic Ga-P bond distances at Ga(2) (av 2.493(2) Å) to be larger than those at Ga(1) (2.410(2) Å). As in the case of 2, the exocyclic metal-phosphorus bond distance (Ga(2)-P(5) = 2.391(3) Å) is shorter than any of the endocyclic metal-phosphorus distances.

Experimental Section

General Considerations. All reactions were performed under oxygen-free argon or under vacuum using standard Schlenk line or drybox techniques. All solvents were dried over sodium and distilled from sodium benzophenone under argon before use. The reagents GaCl₃ and InCl₃ were purchased from Strem Chemicals and used without further purification; *n*-BuLi and *t*-BuLi were purchased from Aldrich Chemicals. The concentrations of the lithium reagents were determined by titrimetric analysis prior to use. The lithium phosphides Li(P-*t*-Bu)₂ and Li(P-*i*-Pr)₂ were prepared by the slow addition of *n*-BuLi to an equimolar amount of the appropriate phosphine at -78 °C, warmed to 25 °C over a 3-4-h period, and used in situ for further reactions. *n*-Bu₂InCl

was prepared by the addition of 2 equiv of *n*-BuLi to InCl₃ in Et₂O or THF solution and used in situ. Literature methods were used for the preparation of *t*-BuGaCl₂¹³ and *i*-PrInI₂.¹⁴

Physical Measurements. IR spectra were obtained on a Perkin-Elmer 1330 spectrometer. Mass spectra, EI and CI, were run on a Bell and Howell 21-491 instrument, and NMR were run on a GE-300 (¹H, 300.17 MHz; ¹³C, 75.48 MHz; ³¹P, 121.50 MHz). NMR spectra are referenced to C₆D₆, which was dried over 4-Å sieves and distilled prior to use, and the shifts are reported relative to Si(CH₃)₄ (0.00 ppm). Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Melting points were obtained in sealed capillaries under argon (1 atm) and are uncorrected.

Synthesis of [*t*-Bu(*i*-Pr₂P)Ga(μ-P-*i*-Pr₂)₂]₂ (1). A mixture of *t*-BuGaCl₂ (0.76 g, 4.03 mmol) and Li(*i*-Pr₂P) (1.00 g, 8.06 mmol) in 50 mL of THF was stirred for 1 h at -78 °C before being allowed to warm slowly to 25 °C. Following an additional 6 h of stirring at 25 °C, the solvent was removed in vacuo, and the resulting white solid was extracted with 45 mL of hexane. After filtration, the solvent was removed from the filtrate under reduced pressure, resulting in a 68% yield of white, microcrystalline [*t*-Bu(*i*-Pr₂P)Ga(μ-P-*i*-Pr₂)₂]₂ (mp: 99-101 °C). ¹H NMR (C₆D₆): δ 2.59 (m, 4 H, μ-PCH), 1.48-1.25 (m, 6 H, P-CH(CH₃)₂), 1.42 (m, 18 H, Ga-C(CH₃)₃). ³¹P NMR (C₆D₆): δ 13.04 (s, *i*-Pr₂P), -22.07 (s, μ-*i*-Pr₂P). MS (CI): 635 (M⁺ - 2*i*-Pr). Anal. Calcd for C₃₂H₇₄Ga₂P₄: C, 53.21; H, 10.33. Found: C, 53.62; H, 10.89.

Synthesis of [*i*-Pr(*i*-Pr₂P)In(μ-P-*i*-Pr₂)₂]₂ (2). A mixture of *i*-PrInI₂ (2.07 g, 5.0 mmol) and Li(*i*-Pr₂P) (1.25 g, 10.1 mmol) in 50 mL of Et₂O was stirred for 1 h at -78 °C and then allowed to warm slowly to 25 °C. Following an additional 3.5 h of stirring at 25 °C, the solvent was removed in vacuo, and the resulting white solid was extracted with 50 mL of toluene. After filtration, the toluene was removed from the filtrate under reduced pressure, and the remaining solid was extracted with 35 mL of Et₂O. Concentration and cooling of the Et₂O solution to -20 °C for 35 days resulted in a 63% yield of clear X-ray quality crystals of [*i*-Pr(*i*-Pr₂P)In(μ-P-*i*-Pr₂)₂]₂ (mp: 144-147 °C dec). ¹H NMR (C₆D₆): δ 2.62 (m, 4 H, μ-PCH), 2.48 (m, 4 H, PCH), 1.70 (m, 12 H, μ-PCH(CH₃)₂), 1.40 (m, 12 H, PCH(CH₃)₂), 1.14 (m, 2 H, InCH). ³¹P NMR (C₆D₆): δ 12.80 (s, *i*-Pr₂P), 3.66 (s, μ-*i*-Pr₂P). MS (CI): 667 (M⁺ - *i*-Pr₂P). Anal. Calcd for C₃₀H₇₀In₂P₄: C, 45.94; H, 8.99. Found: C, 45.35; H, 8.02.

Synthesis of [*t*-Bu(*i*-Pr₂P)Ga(μ-P-*i*-Pr₂)₂Ga(Cl)*t*-Bu] (3). A mixture of *t*-BuGaCl₂ (2.18 g, 11.08 mmol) and Li(*i*-Pr₂P) (2.74 g, 22.14 mmol) in 60 mL of THF was stirred for 1 h at -78 °C and allowed to warm slowly to 25 °C. Following an additional 11 h of stirring at 25 °C, the solvent was removed in vacuo, and the resulting residue was extracted with 50 mL of hexane. After filtration, the filtrate was concentrated and cooled to -20 °C for 7 days, resulting in a 72% yield of clear X-ray quality crystals of [*t*-Bu(*i*-Pr₂P)Ga(μ-*i*-Pr₂)₂Ga(Cl)*t*-Bu] (3) (mp: 160-161 °C). ¹H NMR (C₆D₆): δ 2.59 (m, 4 H, μ-PCH), 2.44 (m, 2 H, PCH), 1.49 (m, 36 H, P-CH(CH₃)₂), 1.43 (m, 18 H, Ga-C(CH₃)₃). ³¹P NMR (C₆D₆): δ 14.81 (s, *i*-Pr₂P), -20.60 (s, μ-*i*-Pr₂P). MS (CI): 638 (M⁺), 524 (M⁺ - 2*t*-Bu). Anal. Calcd for C₂₆H₆₀ClGa₂P₃: C, 48.75; H, 9.44. Found: C, 48.59; H, 9.83.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for 2 and 3 are

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Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for the Non-Hydrogen Atoms of $[\text{i-Pr}(\text{i-Pr}_2\text{P})\text{In}(\mu\text{-P-i-Pr}_2)]_2$ (2)

	x	y	z	U(eq)
In(1)	83178(3)	53776(3)	42759(2)	34(1)
P(1)	9368(1)	3899(1)	55171(9)	32(2)
P(2)	7572(1)	4347(1)	2795(1)	39(4)
C(1)	7106(6)	6827(4)	4629(3)	37(18)
C(2)	6788(8)	7624(8)	3945(6)	100(23)
C(3)	6161(7)	6477(6)	4952(6)	77(14)
C(4)	8727(5)	4024(5)	6497(4)	44(4)
C(5)	7389(6)	3613(6)	6300(5)	61(8)
C(6)	8868(6)	5265(6)	6844(4)	57(7)
C(7)	9111(6)	2345(5)	5184(4)	43(11)
C(8)	9538(6)	2087(6)	4359(4)	56(11)
C(9)	9706(7)	1502(6)	5927(5)	67(20)
C(10)	7049(6)	5597(5)	2030(4)	49(8)
C(11)	8124(7)	6382(6)	2004(4)	66(16)
C(12)	6463(8)	5134(7)	1116(4)	71(23)
C(13)	6063(5)	3649(6)	2801(4)	49(8)
C(14)	6254(7)	2661(7)	3464(5)	79(8)
C(15)	5041(6)	4450(7)	2915(5)	76(22)

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for the Non-Hydrogen Atoms of $[\text{t-Bu}(\text{i-Pr}_2\text{P})\text{Ga}(\mu\text{-P-i-Pr}_2)_2\text{Ga}(\text{Cl})\text{t-Bu}]$ (3)

	x	y	z	U(eq)
Ga(1)	3412(1)	2263(1)	3429(1)	44(1)
Ga(2)	1878(1)	1257(1)	2015(1)	42(1)
P(3)	2414(1)	538(2)	3211(1)	42(1)
P(4)	3097(1)	2569(2)	2226(1)	41(1)
P(5)	1917(1)	-760(2)	1340(1)	53(1)
Cl(1)	2795(1)	4075(2)	3705(1)	56(1)
C(1)	2991(5)	4451(8)	1969(4)	54(4)
C(2)	2889(5)	4617(10)	1207(4)	84(5)
C(21)	2140(6)	8(10)	569(4)	73(4)
C(11)	2752(5)	-1312(8)	3284(5)	66(4)
C(4)	4439(4)	2308(10)	4110(4)	59(4)
C(8)	1822(5)	883(10)	3787(4)	62(4)
C(14)	973(4)	2566(9)	1829(4)	57(4)
C(3)	3613(5)	5429(9)	2373(4)	74(4)
C(15)	1023(5)	3657(10)	2371(5)	87(5)
C(7)	4341(5)	2062(11)	4791(4)	91(5)
C(6)	4766(5)	3781(11)	4083(5)	94(5)
C(5)	5002(5)	1270(12)	3993(5)	102(5)
C(24)	917(5)	-1423(11)	1003(5)	78(5)
C(9)	1075(5)	155(13)	3607(5)	109(6)
C(10)	2232(6)	748(13)	4521(4)	113(6)
C(16)	256(5)	1728(11)	1738(6)	120(7)
C(17)	895(6)	3314(12)	1183(5)	100(5)
C(18)	3798(4)	1745(10)	1849(4)	59(4)
C(20)	4550(5)	2504(10)	1985(5)	84(5)
C(19)	3927(5)	209(9)	2097(5)	75(4)
C(26)	617(6)	-1895(10)	1585(5)	101(6)
C(23)	2636(7)	-1045(13)	301(5)	121(7)
C(25)	868(6)	-2661(11)	509(5)	111(6)
C(13)	2146(6)	-2396(9)	3185(6)	110(6)
C(22)	1483(7)	551(12)	-1(5)	108(6)
C(12)	3390(6)	-1658(11)	3858(6)	135(7)

given in Table III. Atomic coordinates and equivalent isotropic thermal parameters for 2 and 3 are presented in Tables IV and V, respectively. The crystals were mounted in thin-walled glass capillaries and sealed under argon. The unit cell parameters were obtained by centering 25 reflections having 2θ values between 20 and 26°. The data set for 2 was collected on an Enraf-Nonius CAD-4 diffractometer, while those for 3 were collected on a Siemens P3 diffractometer. Both diffractometers used graphite monochromated Mo K α radiation, and the 2θ range for both compounds was between 2 and 50°. The intensity data were recorded in a manner described previously.¹⁵ The observed structure factors of equivalent reflections were averaged, and data with intensities less than $3.0\sigma(I)$ and $(\sin \theta)/\lambda$ less than 0.10 were excluded. For each structure, the data were corrected for

Table VI. Selected Bond Lengths (\AA) and Angles (deg) for $[\text{i-Pr}(\text{i-Pr}_2\text{P})\text{In}(\mu\text{-P-i-Pr}_2)]_2$ (2) and $[\text{t-Bu}(\text{i-Pr}_2\text{P})\text{Ga}(\mu\text{-P-i-Pr}_2)_2\text{Ga}(\text{Cl})\text{t-Bu}]$ (3)

Distances for Compound 2			
In(1)-P(1)	2.642(1)	In(1)-P(2)	2.574(1)
In(1)-C(1)	2.302(5)	P(1)-C(4)	1.871(5)
P(1)-C(7)	1.856(5)	P(2)-C(10)	1.873(6)
P(2)-C(13)	1.883(6)		
Distances for Compound 3			
Ga(1)-P(3)	2.410(2)	Ga(1)-P(4)	2.409(2)
Ga(1)-Cl(1)	2.230(3)	Ga(1)-C(4)	2.009(7)
Ga(2)-P(3)	2.486(2)	Ga(2)-P(4)	2.498(2)
Ga(2)-P(5)	2.389(3)	Ga(2)-P(4)	2.029(8)
P(3)-C(11)	1.859(8)	P(3)-P(8)	1.866(10)
P(4)-C(1)	1.862(8)	P(4)-C(18)	1.867(10)
P(5)-C(21)	1.909(11)	P(5)-C(24)	1.882(10)
Angles for Compound 2			
P(1)-In(1)-P(1)'	107.3(8)	P(1)-In(1)-P(2)	111.83(5)
P(1)-In(1)-C(1)	117.7(2)	P(2)-In(1)-C(1)	118.0(1)
In(1)-P(1)-In(1)'	72.6(1)	In(1)-P(1)-C(4)	112.0(2)
In(1)-P(1)-C(7)	113.0(2)	C(4)-P(1)-C(7)	104.1(3)
In(1)-P(2)-C(10)	102.8(2)	In(1)-P(2)-C(13)	106.4(2)
C(10)-P(2)-C(10)	100.6(3)	In(1)-C(1)-C(3)	116.7(4)
In(1)-C(1)-C(2)	109.7(4)		
Angles for Compound 3			
P(3)-Ga(1)-P(4)	87.0(1)	P(3)-Ga(1)-Cl(1)	98.9(1)
P(4)-Ga(1)-Cl(1)	100.7(1)	P(3)-Ga(1)-C(4)	131.3(3)
P(4)-Ga(1)-C(4)	128.4(3)	Cl(1)-Ga(1)-C(4)	104.5(3)
P(3)-Ga(2)-P(4)	83.4(1)	P(3)-Ga(2)-P(5)	107.0(1)
P(4)-Ga(2)-P(5)	109.0(1)	P(3)-Ga(2)-C(14)	115.2(3)
P(4)-Ga(2)-C(14)	112.1(2)	P(5)-Ga(2)-C(14)	123.0(1)
Ga(1)-P(3)-Ga(2)	93.4(1)	Ga(1)-P(3)-C(11)	114.2(3)
Ga(2)-P(3)-C(11)	111.6(3)	Ga(1)-P(3)-C(8)	108.5(3)
Ga(2)-P(3)-C(8)	116.9(3)	C(11)-P(3)-C(8)	111.1(4)
Ga(1)-P(4)-Ga(2)	93.2(1)	Ga(1)-P(4)-C(1)	112.7(3)
Ga(2)-P(4)-C(1)	114.6(3)	Ga(1)-P(4)-C(18)	113.3(3)
Ga(2)-P(4)-C(18)	114.5(3)	C(1)-P(4)-C(18)	108.2(4)
Ga(2)-P(5)-C(21)	103.5(3)	Ga(2)-P(5)-C(24)	107.1(3)

Lorentz and polarization effects. The structures were solved by direct and Patterson methods and successive cycles of difference maps followed by least squares refinements. All calculations were performed on a MICROVAX 3100 computer using the SHELX programs¹⁶ for 2 and using Siemens SHELXTL PLUS for 3.

$[\text{i-Pr}(\text{i-Pr}_2\text{P})\text{In}(\mu\text{-P-i-Pr}_2)]_2$ (2). Colorless crystals of 2 suitable for X-ray diffraction were grown by cooling an Et₂O solution to -30 °C for 35 days. The space group $P2_1/c$ was uniquely determined by the systematic absences; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. A ψ scan of three reflections having χ values between 80 and 90° showed a minimum transmission factor of 87.9% and a maximum transmission factor of 99.2%, and hence no absorption correction was applied. A set of three intensity standards showed <2% decay over the course of the data collection. The indium atoms were found using a Patterson search, and the location of the non-hydrogen atoms was achieved using difference Fourier electron density maps. The hydrogen atoms were placed in calculated positions and refined using fixed isotropic thermal parameters. The structure was refined to final values of 0.0401 and 0.0509 for R and R_w , respectively.

$[\text{t-Bu}(\text{i-Pr}_2\text{P})\text{Ga}(\mu\text{-P-i-Pr}_2)_2\text{Ga}(\text{Cl})\text{t-Bu}]$ (3). Colorless cubic crystals of 3 suitable for X-ray diffraction were grown by cooling a hexane solution to -30 °C for 7 days. The space group $P2_1/c$ was uniquely determined by the systematic absences; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. A ψ scan of three reflections having χ values between 80 and 90° showed a minimum transmission factor of 89.5% and a maximum transmission factor of 98.3%, and hence no correction was applied. A set of three intensity standards showed <2% decay over the course of the

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data collection. The location of the non-hydrogen atoms was achieved from difference Fourier electron density maps. The hydrogen atoms were placed in calculated positions and refined using fixed isotropic thermal parameters. The structure was refined to final values of 0.0511 and 0.0547 for R and R_w , respectively.

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Supplementary Material Available: Tables of atomic parameters, thermal parameters, and bond distances and angles for 2 and 3 (10 pages). Ordering information is given on any current masthead page.

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