$= \sum||F_o| - |F_c||/\sum|F_o|$, for $F_o^2 > 0$, and the goodness of fit is equal to $[\sum w(F_o^2 - F_c^2)^2/(n = p)]^{1/2}$, where n is the number of data and p is the number of parameters refined. The variances of the individual reflections were assigned on the basis of counting statistics plus an additional term, $0.0141I^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $0.014I^2$.

Acknowledgment. The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Center for Space Microelectronics Technology, which is supported by the Strategic Defense Initiative Organization, Innovative Science and Technology Office, through an agreement with the National Aeronautics and Space Administration. S.R.M. thanks Professor Robert Grubbs for access to synthetic facilities at Caltech. We thank Richard E. Marsh for his persistence in finding the correct structure in the initial Fourier map. The diffractometer used in this study was purchased with a grant from the National Science Foundation (No. CHE-8219039). We thank Paul Groves and Kelly Perry for technical assistance.

Supplementary Material Available: An ORTEP drawing of the cation with atom numbering and tables of crystal data, final parameters of all the atoms, and complete distances and angles (6 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Diphenylphosphide Derivatives of Dineopentylgallium and -indium. Crystal and Molecular Structures of $[(Me_3CCH_2)_2GaPPh_2]_2$ and $[(Me_3CCH_2)_2InPPh_2]_3$

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Received October 30, 1990

The two compounds $(Me_3CCH_2)_2MPPh_2$ (M = Ga, In) have been prepared by metathetical reactions between $(Me_3CCH_2)_2MCl$ and $KPPh_2$ and fully characterized. The characterization data include elemental analyses (C, H), melting points, IR and ^1H and ^{31}P NMR spectral studies, cryoscopic molecular weight studies in benzene solution, and single-crystal X-ray structural studies. The gallium compound exists as a dimer in benzene solution and in the solid state. The corresponding indium derivative exists as a monomer–dimer equilibrium mixture in benzene solution and as a trimer in the solid state. Thus, $(Me_3CCH_2)_2InPPh_2$ represents an unusual example of an amphoteric compound that exhibits three different degrees of association. $[(Me_3CCH_2)_2GaPPh_2]_2$ crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 11.076$ (3) Å, $b = 18.996$ (3) Å, $c = 21.753$ (5) Å, $\beta = 100.128$ (9)°, $V = 4505$ (2) Å^3, and $Z = 4$ (dimeric molecules). The molecule contains a buckled Ga_2P_2 core (dihedral angles of 142.2° across P(1)···P(2) and 145.6° across Ga(1)···Ga(2)); Ga–P distances are in the range 2.479 (3)–2.512 (3) Å, and Ga–C(neopentyl) bond lengths are in the range 1.996 (12)–2.016 (12) Å. $[(Me_3CCH_2)_2InPPh_2]_3$ crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148); unit cell parameters (hexagonal setting) are $a = 20.873$ (5) Å, $c = 29.037$ (4) Å, $V = 10956$ (4) Å^3, and $Z = 6$ (trimeric molecules). The molecules lie on sites of C_3 symmetry, their In_3P_3 cores having a chair conformation. The independent In–P distances are 2.677 (1) and 2.699 (2) Å; In–C(neopentyl) bond lengths are 2.182 (6) and 2.210 (7) Å.

Introduction

The formation of group 13–15 materials such as GaAs and InP from single-source precursors of the type $R_2MER'_2$ (M = group 13 element, E = group 15 element)[1] has provided the motivation to understand more fully the chemistry of this class of compounds. Since the most desirable compounds for preparing group 13–group 15 materials by organometallic chemical vapor deposition (OMCVD) are volatile liquids, our goal has been to study the factors that control the degree of association of these Lewis amphoteric species, their structures, and their physical properties. Some representative examples of monomers are $(C_5Me_5)_2GaAs(SiMe_3)_2$[2] and $t\text{-}Bu_2GaAsBu^t_2$,[3] those of dimers are $(Me_2GaPBu^t_2)_2$,[4] $(Me_2InPBu^t_2)_2$,[5] and $[(Me_3SiCH_2)_2InPPh_2]_2$,[6] and those of trimers are $(Et_2GaPEt_2)_3$[7] and $[Cl_2GaAs(CH_2SiMe_3)_2]_3$.[8] These examples might suggest that steric effects provide an important factor for controlling the degree of association. However, other factors[9] including valency angle strain,

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mechanism of formation, and solvation effects might also be significant. It is noteworthy that most dimers have planar rings but examples with puckered rings have been observed also. In the case of trimers, planar, boat, twist-boat, and irregular boat structures have been observed. Apparently, these rings involving group 13–group 15 elements are sufficiently flexible to accommodate a variety of different conformations.

In this paper we report the synthesis and characterization of $(Me_3CCH_2)_2GaPPh_2$ and $(Me_3CCH_2)_2InPPh_2$. Neopentyl group 13 derivatives are of interest because $In(CH_2CMe_3)_3$ has been used to make InP and InSb of electronic quality by OMCVD.[10,11] The new group 13–group 15 compounds were synthesized by metathesis reactions. The characterization data include elemental analyses (C, H), melting points, ^1H and ^{31}P NMR spectral studies, cryoscopic molecular weight studies, and single-crystal X-ray structural studies. The gallium derivative exists as a dimer in benzene solution and in the solid phase. In contrast, the indium compound is a monomer–dimer equilibrium mixture in benzene solution, whereas a trimer is observed in the crystalline phase.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and water and were manipulated in a standard vacuum line or under a purified argon atmosphere. All solvents were purified before use. Dineopentylgallium chloride[12] and dineopentylindium chloride[13] were prepared as previously described. Diphenylphosphine was purchased from Strem Chemicals, Inc., and was purified by distillation prior to use. Potassium diphenylphosphide[14] ($KPPh_2$) was prepared from diphenylphosphine and excess KH in diethyl ether. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak), and sh (shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ as δ 0.00 and benzene as δ 7.13. The ^{31}P NMR spectra were recorded at 36.23 MHz by using a JEOL FX-90Q spectrometer. The proton-decoupled spectra are reported relative to 85% H_3PO_4 as δ 0.00. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[15]

Synthesis of $(Me_3CCH_2)_2GaPPh_2$. The compound $(Me_3CCH_2)_2GaPPh_2$ was synthesized by a metathesis reaction by using 0.804 g (3.58 mmol) of $KPPh_2$ and 0.888 g (3.59 mmol) of $Ga(CH_2CMe_3)_2Cl$ in 50 mL of Et_2O. $KPPh_2$ was added to the solution of $Ga(CH_2CMe_3)_2Cl$ at −78 °C, and then the mixture was warmed to room temperature. After the solvent had been removed by vacuum distillation, the product was separated by extraction with pentane. The pentane-insoluble off-white solid (0.192 g, 2.58 mmol, 71.9% KCl) was isolated from the frit. The colorless pentane-soluble solid was identified as $(Me_3CCH_2)_2GaPPh_2$ (1.347 g, 3.391 mmol, 94.7% based on $KPPh_2$). Colorless crystals of $(Me_3CCH_2)_2GaPPh_2$ (0.866 g, 2.18 mmol, 60.8% based on $KPPh_2$) were obtained by slow crystallization from a saturated pentane solution maintained at 20 °C. Crystallographic-quality crystals were obtained from a saturated methylcyclohexane solution maintained at −15 °C.

Table I. Experimental Data for the X-ray Diffraction Studies of $[(Me_3CCH_2)_2GaPPh_2]_2$ and $[(Me_3CCH_2)_2InPPh_2]_3$

(A) Unit Cell Parameters

	Ga dimer	In trimer
cryst syst	monoclinic	rhombohedral (hexagonal setting)
space group	$P2_1/n$ (No. 14, var)	$R\bar{3}$ (No. 148)
a, Å	11.076 (2)	20.873 (5)
b, Å	18.996 (3)	20.873 (5)
c, Å	21.753 (5)	29.037 (4)
α, deg	90	90
β, deg	100.128 (9)	90
γ, deg	90	120
V, $Å^3$	4505 (2)	10956 (4)
Z	4 (dimers)	6 (trimers)
formula	$C_{44}H_{64}Ga_2P_2$	$C_{66}H_{96}In_3P_3$
mol wt	794.3	1326.7
D(calcd), g cm^{-3}	1.17	1.21
temp, °C (K)	21 (294)	24 (297)

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo $K\bar{\alpha}$ ($\bar{\lambda}$ = 0.710730 Å)
monochromator: pyrolytic graphite ($2\theta_m$ = 12.160°), equatorial mode, assumed 50% perfect/50% mosaic for polarizn correction
reflns measd: (a) Ga dimer, $+h, +k, \pm l$ for 2θ = 4.5–45.0°, 4757 total reflns, yielding 4398 unique data ($R(I)$ = 4.5% for 359 groups of averaged data); (b) In trimer, $+h, \pm k, \pm l$ for 2θ = 4.5–45.0°, 10215 rflns, yielding 3214 unique data ($R(I)$ = 3.1% for averaging of three forms)
scan type: θ(cryst)–2θ(counter) at 4.0°/min in 2θ from $[2\theta(K\alpha_1) - \Delta]°$ to $[2\theta(K\alpha_2) + \Delta]°$ (Δ = 1.0° for Ga dimer and 0.8° for In trimer)
bkgds: stationary cryst and counter at each end of the 2θ scan, each for $^1/_4$ of total scan time
std rflns: 3 approximately mutually orthogonal rflns collected after each batch of 97 data; substantial decay was obsd and corrected for the Ga dimer (see text); neither significant fluctuations nor decay were observed for the In trimer
abs cor: (a) Ga dimer, μ = 13.6 cm^{-1}, data corrected empirically by interpolation in 2θ and ϕ between transmission curves (ψ scans) of four close-to-axial reflections (T_{min}/T_{max} = 0.75); (b) In trimer, μ = 10.3 cm^{-1}, 5 close-to-axial ψ scans (T_{min}/T_{max} = 0.87)

$(Me_3CCH_2)_2GaPPh_2$. Mp: 157–160 °C dec (glass transition, 132–135 °C). ^1H NMR (C_6H_6, δ): 1.10 (s, 18 H, $-CMe_3$), 1.39 (t, $^3J_{PGaCH}$ = 3.6 Hz, 4.2 H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6, δ): −25.9 (s, 0.024–0.403 *m*). Anal. Calcd: C, 66.52; H, 8.14. Found: C, 66.83; H, 8.08. Cryoscopic molecular weight, formula weight 397.23 (calculated molality, observed molality, association): 0.07568, 0.0337, 2.25; 0.06626, 0.0299, 2.21; 0.06346, 0.0290, 2.19; 0.04326, 0.0199, 2.18. IR (Nujol mull, cm^{-1}): 3070 (w), 3050 (w), 1942 (vw), 1870 (vw, br), 1800 (vw, br), 1580 (w), 1430 (s), 1354 (s), 1328 (vw), 1300 (vw), 1265 (vw), 1234 (m), 1220 (m), 1175 (vw), 1165 (vw), 1152 (w), 1140 (w), 1131 (w), 1128 (w), 1109 (w), 1102 (w), 1098 (w), 1090 (w), 1065 (w), 1021 (m), 1010 (w), 995 (m), 976 (vw), 960 (vw), 928 (vw), 905 (vw), 886 (vw), 839 (vw), 740 (m), 730 (s), 718 (m), 710 (m), 688 (vs), 675 (m, sh), 602 (m), 580 (vw), 540 (vw), 510 (m), 502 (m), 469 (w), 462 (w), 450 (w), 385 (w), 285 (vw).

Synthesis of $(Me_3CCH_2)_2InPPh_2$. The compound $(Me_3CCH_2)_2InPPh_2$ was synthesized from 0.538 g (1.84 mmol) of $In(CH_2CMe_3)_2Cl$ and 0.412 g (1.84 mmol) of $KPPh_2$. The indium-containing product (0.499 g, 1.13 mmol, 61.5% yield based on $In(CH_2CMe_3)_2Cl$) was isolated by benzene extraction. Crystallographic-quality crystals were obtained by heating a saturated solution to 35 °C and then permitting the solution to slowly cool to room temperature. The characterization data for the compound prepared by the metathetical reaction as described above were similar to the data reported for the compound prepared by the elimination reaction[6] between $In(CH_2CMe_3)_3$ and $P(H)Ph_2$.

Collection of X-ray Diffraction Data for $[(Me_3CCH_2)_2GaPPh_2]_2$. A fragment of approximate size 0.7 × 0.6 × 0.4 mm was cut from a larger crystal and sealed into a thin-walled glass capillary; these manipulations were performed

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under an inert atmosphere (Ar). The capillary was mounted in a brass pin on a eucentric goniometer and was accurately centered on a Syntex $P2_1$ automated four-circle diffractometer. All subsequent operations (determination of orientation matrix and cell parameters, and data collection) were carried out as described previously.[16] Details are presented in Table I.

The crystal belongs to the monoclinic system ($2/m$ diffraction symmetry). The systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) uniquely define the centrosymmetric monoclinic space group $P2_1/n$ (a common variant of $P2_1/c$, No. 14). All data were corrected for decay (linear correction for an ~30% decrease in intensities of the standard reflections), absorption, and Lorentz and polarization factors and were placed on an approximately absolute scale by means of a Wilson plot.

Solution and Refinement of the Structure of $[(Me_3CCH_2)_2GaPPh_2]_2$. All crystallographic calculations were carried out under our locally modified set of Syntex XTL programs. Calculated structure factors were based upon the analytical functions expressing scattering factors for neutral atoms.[17] Both the real ($\Delta f'$) and imaginary $i\Delta f''$) components of anomalous dispersion[18] were included for all non-hydrogen atoms. The function minimized in least-squares refinement was $\sum w(\Delta F)^2$, where $w = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}^{-1}$. Discrepancy indices are defined as

$$R_F\ (\%) = 100\sum||F_o| - |F_c||/\sum|F_o|$$

$$R_{wF}\ (\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

$$\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$$

Here, NO is the number of observations and NV is the number of variables.

The structure was solved by use of MULTAN,[19] which revealed the positions of the heavy atoms. The remaining non-hydrogen atoms were located from a difference-Fourier map. Refinement of positional and thermal parameters (anisotropic for the $[(C_3C-C)_2GaP_2]_2$ moiety and isotropic for carbon atoms of the phenyl groups) and with hydrogen atoms in idealized locations[20] led to convergence with $R_F = 5.7\%$, $R_{wF} = 7.7\%$, and GOF = 1.60 for data with $|F_o| > 6\sigma(|F_o|)$ ($R_F = 10.8\%$ and $R_{wF} = 9.3\%$ for all data). We attribute these rather high values to crystal decomposition in the X-ray beam.

A final difference-Fourier map showed no unexpected features (ρ(max) = 0.47 e/Å^3). Final positional parameters are given in Table II.

Collection of X-ray Diffraction Data for $[(Me_3CCH_2)_2InPPh_2]_3$. A clear colorless parallelepiped of dimensions 0.5 × 0.3 × 0.25 mm was sealed (under Ar) into a capillary and mounted as for the previous study (vide supra). Crystal data are compiled in Table I.

The crystal is rhombohedral, with $\bar{3}$ symmetry (rather than $\bar{3}m$). In the triply primitive obverse hexagonal setting, the only systematic absences are for $-h + k + l \neq 3n$. Possible space groups are the noncentrosymmetric $R3$ (C_3, No. 146) and the centrosymmetric $R\bar{3}$ (C_{3i}, No. 148).[21] The latter is more probable with $Z = 6$ (trimeric units) and was confirmed by the successful solution in this higher symmetry space group. Data for three equivalent forms were collected. Following correction for absorption, these were merged to a unique set ($R(I) = 3.1\%$), were corrected for Lorentz and polarization factors, and were placed on an approximately absolute scale by means of a Wilson plot. Intensity statistics were in keeping with the centric case.

Solution and Refinement of the Structure of $[(Me_3CCH_2)_2InPPh_2]_3$. The structure was solved by means of a Patterson synthesis, which revealed the location of the crystallographically unique indium atom. Difference-Fourier syntheses led to the location of all non-hydrogen atoms and most hydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, with all hydrogen atoms included in idealized locations[20] (d(C–H) = 0.95 Å, staggered-tetrahedral or externally bisecting trigonal geometry), led to convergence with $R_F = 4.6\%$, $R_{wF} = 5.3\%$, and GOF = 1.21 for all 3214 data ($R_F = 3.2\%$, $R_{wF} = 4.9\%$ for those 2436 data with $|F_o| > 6\sigma(|F_o|)$).

Table II. Final Positional Parameters for $[(Me_3CCH_2)_2GaPPh_2]_2$

atom	*x*	*y*	*z*	*B*, Å^2
Ga(1)	1.029 66 (11)	0.224 46 (7)	0.081 52 (6)	
Ga(2)	0.781 46 (11)	0.285 59 (7)	0.154 67 (6)	
P(1)	1.008 24 (26)	0.280 97 (17)	0.181 95 (13)	
P(2)	0.816 08 (27)	0.184 06 (16)	0.087 61 (15)	
C(11)	0.995 3 (10)	0.287 06 (64)	0.006 75 (55)	
C(12)	1.080 3 (12)	0.349 03 (66)	−0.003 61 (57)	
C(13)	1.207 5 (16)	0.327 5 (10)	0.000 5 (12)	
C(14)	1.072 5 (17)	0.407 11 (80)	0.042 83 (73)	
C(15)	1.036 4 (16)	0.381 42 (89)	−0.068 26 (69)	
C(21)	1.172 7 (11)	0.159 22 (63)	0.099 96 (58)	
C(22)	1.198 1 (12)	0.100 18 (75)	0.057 10 (70)	
C(23)	1.112 7 (19)	0.039 7 (11)	0.063 0 (12)	
C(24)	1.163 2 (26)	0.119 0 (12)	−0.011 1 (11)	
C(25)	1.321 9 (15)	0.069 5 (10)	0.073 21 (85)	
C(31)	0.701 2 (11)	0.286 36 (67)	0.230 95 (56)	
C(32)	0.600 5 (11)	0.234 35 (64)	0.242 55 (57)	
C(33)	0.502 0 (15)	0.228 2 (10)	0.183 69 (76)	
C(34)	0.538 7 (14)	0.263 8 (10)	0.294 26 (76)	
C(35)	0.649 4 (13)	0.161 42 (79)	0.262 90 (67)	
C(41)	0.752 7 (10)	0.362 13 (57)	0.090 51 (55)	
C(42)	0.671 5 (12)	0.426 39 (72)	0.094 68 (65)	
C(43)	0.667 4 (12)	0.473 28 (75)	0.037 06 (75)	
C(44)	0.542 5 (15)	0.405 7 (10)	0.098 5 (10)	
C(45)	0.724 6 (18)	0.470 04 (88)	0.150 86 (91)	
C(51)	1.062 3 (10)	0.221 82 (57)	0.245 83 (48)	2.94 (22)
C(52)	0.983 7 (13)	0.178 43 (74)	0.271 49 (65)	5.49 (33)
C(53)	1.025 4 (16)	0.133 48 (88)	0.320 71 (79)	7.71 (43)
C(54)	1.145 4 (15)	0.127 73 (81)	0.346 17 (70)	6.72 (38)
C(55)	1.223 1 (16)	0.171 66 (95)	0.321 76 (81)	8.04 (44)
C(56)	1.184 1 (14)	0.217 43 (78)	0.272 47 (69)	6.32 (35)
C(61)	1.088 2 (10)	0.362 87 (56)	0.208 34 (48)	2.94 (24)
C(62)	1.207 2 (13)	0.374 32 (74)	0.201 64 (63)	5.54 (33)
C(63)	1.266 0 (14)	0.438 85 (88)	0.220 76 (74)	7.16 (40)
C(64)	1.201 2 (15)	0.488 09 (89)	0.246 73 (77)	7.57 (42)
C(65)	1.087 4 (15)	0.478 67 (87)	0.254 85 (75)	7.61 (42)
C(66)	1.026 6 (12)	0.413 31 (70)	0.235 58 (62)	4.96 (31)
C(71)	0.790 4 (10)	0.094 65 (57)	0.115 34 (52)	3.17 (25)
C(72)	0.677 2 (11)	0.060 88 (62)	0.096 99 (55)	4.01 (28)
C(73)	0.659 0 (12)	−0.006 15 (68)	0.121 66 (60)	4.71 (30)
C(74)	0.749 1 (13)	−0.038 94 (70)	0.159 80 (64)	5.38 (33)
C(75)	0.860 1 (13)	−0.008 65 (76)	0.178 56 (65)	5.84 (34)
C(76)	0.881 3 (12)	0.059 47 (69)	0.156 43 (61)	4.88 (31)
C(81)	0.714 3 (10)	0.185 83 (56)	0.012 23 (49)	2.77 (23)
C(82)	0.600 4 (12)	0.214 15 (66)	0.005 25 (58)	4.72 (29)
C(83)	0.520 0 (13)	0.211 90 (78)	−0.055 63 (69)	6.42 (36)
C(84)	0.561 7 (13)	0.180 55 (76)	−0.104 79 (67)	6.05 (35)
C(85)	0.673 6 (14)	0.152 30 (75)	−0.097 42 (69)	6.15 (35)
C(86)	0.752 2 (11)	0.155 51 (65)	−0.038 70 (57)	4.21 (28)

A final difference-Fourier map was essentially featureless (ρ(max) = 0.40 e/Å^3, ~0.6 Å from In). Positional parameters are collected in Table III.

Lewis Acidity–Basicity Studies of $(Me_3CCH_2)_2GaPPh_2$. Phosphorus-31 NMR spectroscopy was used to investigate the Lewis acidity–basicity of $(Me_3CCH_2)_2GaPPh_2$ toward Et_2O, THF, NMe_3, and $Ga(CH_2CMe_3)_3$. No stable (isolable) adducts could be isolated at room temperature. The only reagent that produced spectroscopic data indicative of a Lewis acid–base interaction was NMe_3. All other reagent combinations provided ^{31}P NMR spectra that had a line at −25.1 ppm indicative of $[(Me_3CCH_2)_2GaPPh_2]_2$. When an aliquot of a solution prepared by combining 0.137 g (0.346 mmol) of $(Me_3CCH_2)_2GaPPh_2$, 0.211 g (3.57 mmol) of NMe_3, and 4 mL of C_6H_6 was studied, lines were observed at −25.1 ppm (s, 4.21) and at −43.7 ppm (s, 1.00). Removal of NMe_3 and C_6H_6 from the remainder of the original solution afforded a colorless solid whose solution in benzene exhibited only one line at −25.1 ppm ($(Me_3CCH_2)_2GaPPh_2$) in the ^{31}P NMR spectrum.

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Table III. Final Positional Parameters for $[(Me_3CCH_2)_2InPPh_2]_3$

atom	*x*	*y*	*z*
In	0.117 01 (2)	0.143 04 (2)	0.228 86 (1)
P	0.124 40 (7)	0.023 28 (6)	0.204 37 (5)
C(1)	0.109 09 (32)	0.118 39 (33)	0.302 34 (20)
C(2)	0.163 89 (37)	0.169 65 (37)	0.339 57 (21)
C(3)	0.159 05 (45)	0.239 62 (49)	0.344 53 (30)
C(4)	0.243 68 (40)	0.192 60 (45)	0.325 19 (29)
C(5)	0.142 79 (63)	0.128 99 (62)	0.384 61 (28)
C(6)	0.185 72 (39)	0.226 18 (35)	0.176 60 (26)
C(7)	0.224 83 (34)	0.308 16 (31)	0.184 68 (28)
C(8)	0.170 40 (49)	0.331 98 (41)	0.200 28 (41)
C(9)	0.264 33 (75)	0.349 88 (50)	0.142 99 (37)
C(10)	0.285 17 (61)	0.329 83 (57)	0.220 49 (64)
C(11)	0.146 12 (26)	0.027 20 (26)	0.142 29 (19)
C(12)	0.190 21 (33)	0.000 29 (36)	0.125 17 (20)
C(13)	0.201 44 (42)	0.001 34 (46)	0.077 67 (25)
C(14)	0.169 01 (39)	0.026 92 (46)	0.047 44 (22)
C(15)	0.124 96 (36)	0.053 17 (38)	0.064 43 (22)
C(16)	0.114 16 (28)	0.053 88 (30)	0.111 71 (19)
C(21)	0.212 27 (27)	0.045 77 (26)	0.232 40 (17)
C(22)	0.278 71 (28)	0.106 86 (31)	0.218 30 (20)
C(23)	0.344 34 (30)	0.127 11 (37)	0.241 38 (24)
C(24)	0.343 72 (34)	0.088 06 (40)	0.279 58 (26)
C(25)	0.279 63 (36)	0.028 21 (36)	0.293 82 (26)
C(26)	0.214 00 (30)	0.006 43 (30)	0.270 20 (21)

Table IV. Interatomic Distances (Å) for $[(Me_3CCH_2)_2GaPPh_2]_2$

(A) Gallium-Phosphorus Distances			
Ga(1)-P(1)	2.482 (3)	Ga(2)-P(2)	2.488 (3)
Ga(1)-P(2)	2.512 (3)	Ga(2)-P(1)	2.479 (3)
(B) Gallium-Carbon Distances			
Ga(1)-C(11)	1.997 (12)	Ga(2)-C(31)	2.016 (12)
Ga(1)-C(21)	1.996 (12)	Ga(2)-C(41)	2.002 (11)
(C) Phosphorus-Carbon Distances			
P(1)-C(51)	1.805 (11)	P(2)-C(71)	1.841 (11)
P(1)-C(61)	1.832 (11)	P(2)-C(81)	1.820 (11)
(D) Neopentyl Carbon-Carbon Distances			
C(11)-C(12)	1.548 (17)	C(31)-C(32)	1.544 (18)
C(12)-C(13)	1.454 (22)	C(32)-C(33)	1.533 (20)
C(12)-C(14)	1.509 (20)	C(32)-C(34)	1.522 (21)
C(12)-C(15)	1.534 (20)	C(32)-C(35)	1.525 (19)
C(21)-C(22)	1.516 (19)	C(41)-C(42)	1.528 (18)
C(22)-C(23)	1.508 (26)	C(42)-C(43)	1.532 (21)
C(22)-C(24)	1.510 (27)	C(42)-C(44)	1.498 (22)
C(22)-C(25)	1.474 (22)	C(42)-C(45)	1.508 (23)

Results and Discussion

The two compounds $(Me_3CCH_2)_2GaPPh_2$ and $(Me_3CCH_2)_2InPPh_2$[6] have been prepared by metathetical reactions from the appropriate neopentylmetal halide derivative and $KPPh_2$ and have been fully characterized. The characterization data include elemental analyses, cryoscopic molecular weight measurements in benzene solution, IR and ^1H and ^{31}P NMR spectroscopic data, and single-crystal X-ray structural studies. The indium derivative was previously described,[6] but an X-ray structural study was not reported. It is noteworthy that the gallium compound is dimeric in the solid state and in benzene solution. In contrast, the indium derivative is trimeric in the crystalline state but a monomer-dimer equilibrium mixture in benzene solution.

Table V. Angles (deg) for $[(Me_3CCH_2)_2GaPPh_2]_2$

(A) Angles around the Gallium Atom			
P(1)-Ga(1)-P(2)	81.33 (11)	P(2)-Ga(2)-P(1)	81.88 (11)
P(1)-Ga(1)-C(11)	115.18 (35)	P(2)-Ga(2)-C(31)	128.61 (37)
P(1)-Ga(1)-C(21)	106.67 (37)	P(2)-Ga(2)-C(41)	100.16 (34)
P(2)-Ga(1)-C(11)	100.30 (35)	P(1)-Ga(2)-C(31)	112.22 (36)
P(2)-Ga(1)-C(21)	121.41 (37)	P(1)-Ga(2)-C(41)	102.88 (34)
C(11)-Ga(1)-C(21)	124.35 (50)	C(31)-Ga(2)-C(41)	121.98 (49)
(B) Angles around the Phosphorus Atom			
Ga(1)-P(1)-Ga(2)	93.11 (11)	Ga(2)-P(2)-Ga(1)	92.16 (11)
Ga(1)-P(1)-C(51)	109.77 (36)	Ga(2)-P(2)-C(71)	118.32 (38)
Ga(1)-P(1)-C(61)	121.83 (37)	Ga(2)-P(2)-C(81)	112.27 (37)
Ga(2)-P(1)-C(51)	113.02 (36)	Ga(1)-P(2)-C(71)	120.01 (38)
Ga(2)-P(1)-C(61)	117.28 (36)	Ga(1)-P(2)-C(81)	112.76 (37)
C(51)-P(1)-C(61)	102.17 (50)	C(71)-P(2)-C(81)	101.85 (51)
(C) Gallium-Carbon-Carbon Angles			
Ga(1)-C(11)-C(12)	122.5 (8)	Ga(2)-C(31)-C(32)	124.5 (9)
Ga(1)-C(21)-C(22)	124.2 (9)	Ga(2)-C(41)-C(42)	124.2 (8)
(D) Phosphorus-Carbon-Carbon Angles			
P(1)-C(51)-C(52)	122.3 (9)	P(2)-C(71)-C(72)	120.7 (9)
P(1)-C(51)-C(56)	122.0 (9)	P(2)-C(71)-C(76)	121.1 (9)
P(1)-C(61)-C(62)	121.5 (9)	P(2)-C(81)-C(82)	121.7 (9)
P(1)-C(61)-C(66)	118.7 (9)	P(2)-C(81)-C(86)	119.2 (9)

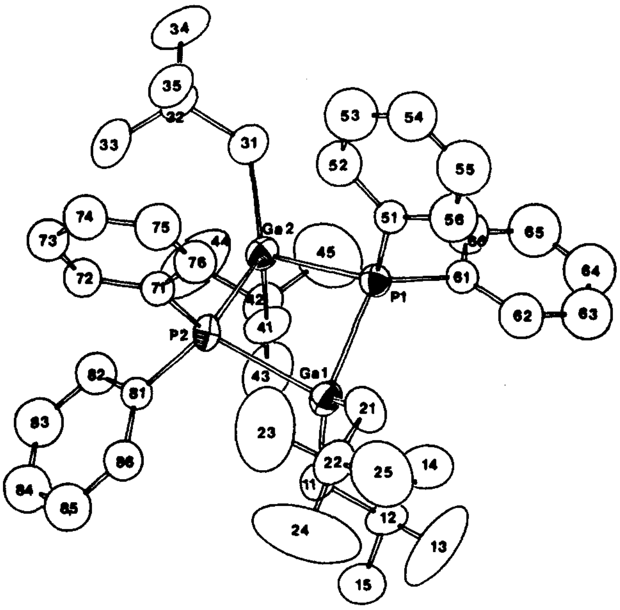

Figure 1. ORTEP diagram for $[(Me_3CCH_2)_2GaPPh_2]_2$, showing the atomic labeling. Carbon atoms are designated by number only.

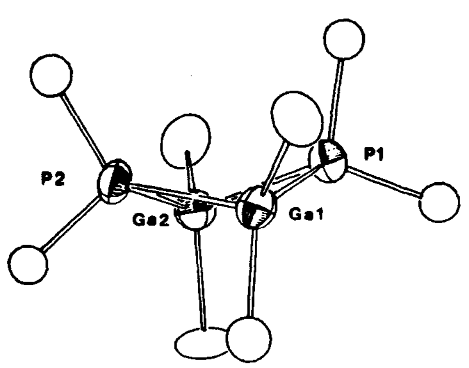

Figure 2. Side-on view of the molecular core of $[(Me_3CCH_2)_2GaPPh_2]_2$.

Crystals of dineopentylgallium diphenylphosphide are composed of discrete dimeric units of composition $[(Me_3CCH_2)_2GaPPh_2]_2$, which are mutually separated by normal van der Waals distances. Distances and angles are provided in Tables IV and V. An ORTEP diagram, showing atomic labeling, is illustrated in Figure 1. Rather surprisingly, the dimeric molecule has a buckled or butterfly ring geometry rather than a planar Ga_2P_2 core. (There is no crystallographic symmetry imposed upon the molecule.) The dihedral angles are Ga(1)-P(1)-Ga(2)/Ga(1)-P(2)-Ga(2) = 142.2° and P(1)-Ga(1)-P(2)/P(1)-Ga(2)-P(2) = 145.6°. A "side on" view of the molecular core is shown in Figure 2. For comparison, $[Bu^n{}_2GaPBu^t{}_2]_2$[4a] and $[Bu^t{}_2GaP(H)(C_5H_9)]_2$[22] have planar Ga_2P_2 rings.

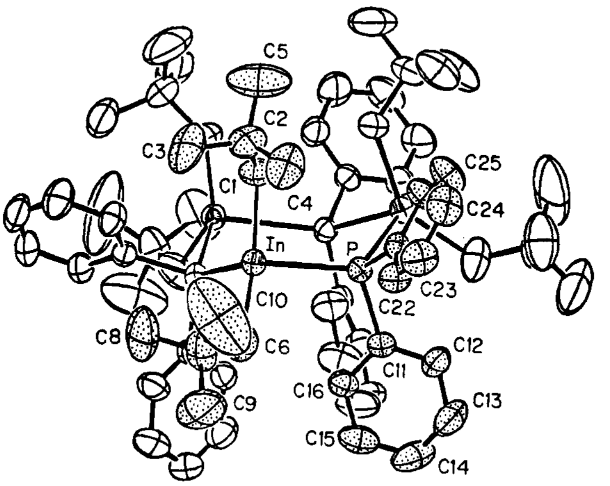

Figure 3. ORTEP diagram for $[(Me_3CCH_2)_2InPPh_2]_3$. The crystallographic asymmetric unit is stippled.

Gallium–phosphorus distances (in increasing order) are Ga(2)–P(1) = 2.479 (3) Å, Ga(1)–P(1) = 2.482 (3) Å, Ga(2)–P(2) = 2.488 (3) Å, and Ga(1)–P(2) = 2.512 (3) Å (average 2.490 ± 0.015 Å). These Ga–P distances are longer than the Ga–P distance in gallium phosphide[23] of 2.360 Å, that in $Ga[P(H)Ar]_3$ (Ar = 2,4,6-$Bu^t{}_3C_6H_2$)[4a] of 2.34 (1) Å, and that in $[Li(THF)_4][Ga(PPh_2)_4]$[24] of 2.409 (7) Å but comparable to the distances in $[Bu^n{}_2GaPBu^t{}_2]_2$[4a] of 2.468 (4)–2.483 (5) Å and the distance in $[Bu^t{}_2GaP(H)(C_5H_9)]_2$[22] of 2.451 (1) Å. The gallium–C(neopentyl) distances (in order) are Ga(1)–C(21) = 1.996 (12) Å, Ga(1)–C(11) = 1.997 (12) Å, Ga(2)–C(41) = 2.002 (11) Å, and Ga(2)–C(31) = 2.016 (12) Å (average 2.003 ± 0.009 Å).

Angles within the Ga_2P_2 ring are acute at gallium (P(1)–Ga(1)–P(2) = 81.33 (11)° and P(2)–Ga(2)–P(1) = 81.88 (11)°) and obtuse at phosphorus (Ga(1)–P(1)–Ga(2) = 93.11 (11)° and Ga(2)–P(2)–Ga(1) = 92.16 (11)°). It seems probable that the buckling of the Ga_2P_2 ring results from steric interactions between the bulky Me_3CCH_2 and/or PPh_2 ligands. The tetrahedral geometry at the gallium(III) atoms is irregular. The small P–Ga–P angles have already been noted. There are some angles substantially increased from the ideal tetrahedral value of 109.47°. Noteworthy are the following: (a) angles between the neopentyl ligands, C(11)–Ga(1)–C(21) = 124.35 (50)° and C(31)–Ga(2)–C(41) = 121.98 (49)°, and (b) one angle, at each gallium atom, between a neopentyl and a diphenylphosphido ligand, P(2)–Ga(1)–C(21) = 121.41 (37)° and P(2)–Ga(2)–C(31) = 128.61 (37)°. The former require no further explanation; the latter involve neopentyl ligands on the crowded "hinged" surface of the Ga_2P_2 core (i.e., the upper surface of Figure 2).

Within the neopentyl ligands, the Ga–C(α)–C(β) angles are expanded from the normal tetrahedral value (a feature general to metal–neopentyl complexes): Ga(1)–C(11)–C(12) = 122.5 (8)°, Ga(1)–C(21)–C(22) = 124.2 (9)°, Ga(2)–C(41)–C(42) = 124.2 (8)°, and Ga(2)–C(31)–C(32) = 124.5 (9)° (average 123.9 ± 0.9°). All other distances and angles are within the normal ranges.

Crystals of dineopentylindium diphenylphosphide are composed of discrete trimeric units of composition $[(Me_3CCH_2)_2InPPh_2]_3$, separated by normal van der Waals distances. The molecules lie on crystallographic 3-fold axes and have crystallographically imposed C_3 symmetry. A single molecule thus encompasses the following equipoints: x, y, z; $-y, x-y, z$; $y-x, -x, z$. The molecular structure is illustrated in Figure 3. Distances and angles are compiled in Tables VI and VII. Figure 4 provides a stereoscopic view of the molecule.

Table VI. Interatomic Distances (Å) for $[(Me_3CCH_2)_2InPPh_2]_3$

(A) Indium–Phosphorus Distances			
In–P	2.677 (1)	In–P ($-y, x-y, z$)	2.699 (2)
(B) Indium–Carbon Distances			
In–C(1)	2.182 (6)	In–C(6)	2.210 (7)
(C) Phosphorus–Carbon Distances			
P–C(11)	1.850 (6)	P–C(21)	1.840 (6)
(D) Neopentyl Carbon–Carbon Distances			
C(1)–C(2)	1.549 (9)	C(6)–C(7)	1.501 (9)
C(2)–C(3)	1.520 (12)	C(7)–C(8)	1.519 (13)
C(2)–C(4)	1.543 (13)	C(7)–C(9)	1.478 (13)
C(2)–C(5)	1.500 (11)	C(7)–C(10)	1.517 (18)

Table VII. Interatomic Angles (deg) for $[(Me_3CCH_2)_2InPPh_2]_3$

(A) Angles about the Indium Atom			
C(1)–In–C(6)	143.11 (26)	P–In–P($-y, x-y, z$)	100.78 (4)
P–In–C(1)	94.16 (17)	C(1)–In–P($-y, x-y, z$)	103.84 (17)
P–In–C(6)	103.49 (20)	C(6)–In–P($-y, x-y, z$)	104.28 (20
(B) Angles about the Phosphorus Atoms			
C(11)–P–C(21)	103.23 (24)	In–P–In($y-x, -x, z$)	125.13 (5)
In–P–C(11)	110.17 (18)	C(11)–P–In($y-x, -x, z$)	109.95 (18)
In–P–C(21)	99.19 (18)	C(21)–P–In($y-x, -x, z$)	106.30 (18)
(C) Indium–Carbon–Carbon Angles			
In–C(1)–C(2)	125.25 (45)	In–C(6)–C(7)	123.89 (52)
(D) Phosphorus–Carbon–Carbon Angles			
P–C(11)–C(12)	121.89 (44)	P–C(21)–C(22)	120.77 (42)
P–C(11)–C(16)	119.08 (42)	P–C(21)–C(26)	121.25 (43)

The In_3P_3 core of the molecule takes up the classical chair conformation (similar to cyclohexane) with strict C_3 symmetry and approximate C_{3v} symmetry. The two independent In–P bond lengths are In–P = 2.677 (1) Å and In–P($-y, x-y, z$) = 2.699 (2) Å, and the two independent intra-ring angles are P–In–P($-y, x-y, z$) = 100.78 (4)° and In–P–In($y-x, -x, z$) = 125.13 (5)°. These In–P distances may be compared to the In–P bond distances in $[(Me_3SiCH_2)_2InPPh_2]_2$[6] of 2.664 (2) and 2.643 (2) Å for molecule "A" and of 2.659 (2) and 2.632 (2) Å for molecule "B", those in $(Me_2InPBu^t{}_2)_2$[5] of 2.637 (4) and 2.656 (4) Å, that in indium phosphide[23,25] of 2.541 (3) Å, and that in $[Li(THF)_4][In(PPh_2)_4]$[24] of 2.576 Å (average). The In–P distances in the adducts $Me_3In{\cdot}P(Ph_2)CH_2CH_2(Ph_2)P{\cdot}InMe_3$[26] of 2.755 (4) Å and those in $Cl_3In{\cdot}2PPh_3$[27] of 2.723 (5) and 2.701 (5) Å are longer than in the trimer. However, the bond distance of 2.683 (4) Å for $Me_3In{\cdot}PMe_3$[26] is comparable. The indium–C(neopentyl) distances are In–C(1) = 2.182 (6) Å and In–C(6) = 2.210 (7) Å (average 2.196 Å).

Both the indium and phosphorus atoms have distorted-tetrahedral environments. The organic groups peripheral to the In_3P_3 core appear to be crowded, but the most dramatic distortions involve the neopentyl groups. The C–In–C angles are greatly distorted from a regular tetrahedral angle, to the value C(1)–In–C(6) = 143.11 (26)°. The In–C(α)–C(β) angles for the neopentyl ligands are

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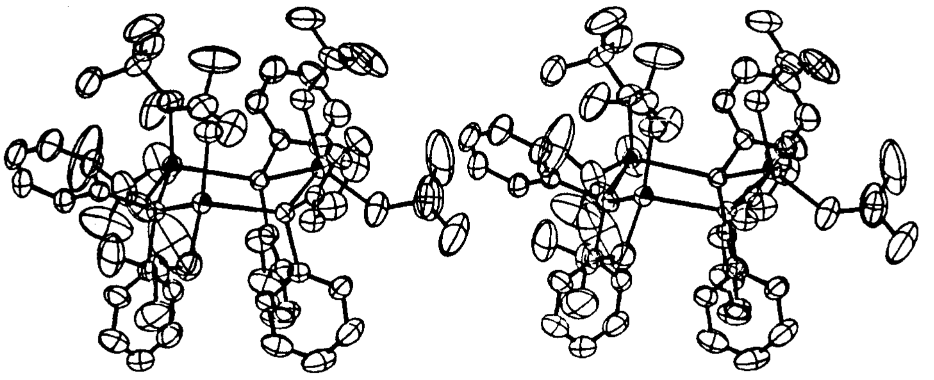

Figure 4. Stereoscopic view of $[(Me_3CCH_2)_2InPPh_2]_3$.

similar to those in the corresponding gallium-phosphorus compound, with In-C(1)-C(2) = 125.25 (45)° and In-C-(6)-C(7) = 123.89 (52)°.

Other features of the interatomic parameters are normal, with P-C = 1.840 (6)-1.850 (6) Å, C-C(phenyl) = 1.360 (10)-1.397 (10) Å (average 1.383 ± 0.011 Å), and C-C-(neopentyl) = 1.478 (13)-1.549 (9) Å (average 1.516 ± 0.023 Å).

The cryoscopic molecular weight measurements in benzene solution permit comparisons of the degrees of association of the compounds in solution and in the solid state. The gallium-phosphorus derivative is a dimer in solution, whereas the indium compound is a monomer-dimer equilibrium mixture, as indicated by the concentration dependence of the molecular weight as well as of the ^1H and ^{31}P NMR spectral data. The observed molecular weight for $[(Me_3CCH_2)_2GaPPh_2]_2$ did not change significantly with concentration, and only one line was observed in the ^{31}P NMR spectrum over the concentration range of 0.024-0.403 *m*. In contrast, as solutions of $(Me_3CCH_2)_2InPPh_2$ were diluted, the molecular weight decreased and the relative intensities of the two ^{31}P NMR lines changed.[6] These observations suggest that thermodynamic factors such as solvation energies and entropic effects rather than kinetic factors influence significantly the degree of association of R_2MER_2 compounds. X-ray structural studies cannot be used with any degree of reliability to predict the degree of association of the amphoteric group 13-group 15 compounds of this type in solution. Since the corresponding (trimethylsilyl)methyl derivatives[6] $(Me_3SiCH_2)_2MPPh_2$ (M = Ga, In) were monomer-dimer equilibrium mixtures, the data suggest the neopentyl substituent is a stronger electron-withdrawing group than the (trimethylsilyl)methyl group and the metal is a correspondingly better Lewis acid.[12,13]

The ^1H NMR spectrum of $[(Me_3CCH_2)_2GaPPh_2]_2$ in benzene (0.024-0.403 *m*) revealed a singlet at 1.10 ppm for the methyl protons of the neopentyl group and a triplet at 1.39 ppm for the methylene protons of the neopentyl group with no dependence on concentration. The triplet with the coupling constant value $^3J_{PGaCH}$ = 3.6 Hz was due to phosphorus-31 coupling by two phosphorus atoms adjacent to a gallium atom as in the dimer. ^{31}P NMR spectral studies in the same concentration range as the ^1H NMR studies revealed only a singlet at -25.0 ppm. The molecular weight data suggest that this line is due to the dimer. Some limited data in the literature[6] for ^{31}P NMR spectra of compounds of the type $R_2MER'_2$ suggested a relationship to exist between δ and the degree of association. For example, the spectra for $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$[6] have lines for the monomer and dimer at -27, -40 and -29, -50 ppm, respectively. This relationship would have erroneously suggested that $(Me_3CCH_2)_2GaPPh_2$ might be monomeric in solution. Thus, ^{31}P NMR spectral data should not be used to predict the degree of association of the compound in solution.

The gallium phosphide $(Me_3CCH_2)_2GaPPh_2$ was reacted with the Lewis bases Et_2O, THF, and NMe_3 and with the Lewis acid $Ga(CH_2CMe_3)_3$ in order to determine if the phosphide was a Lewis acid or base. No stable (isolable) room-temperature adducts were formed. However, the ^{31}P NMR spectra suggested that only NMe_3 was a sufficiently strong base to form an equilibrium mixture with an apparent adduct. The simplest possible adduct would be $Me_3N{\cdot}Ga(CH_2CMe_3)_2PPh_2$, but other adducts involving partially dissociated dimers and rapid equilibria cannot be discounted:

$$[(Me_3CCH_2)_2GaPPh_2]_2 + 2NMe_3 \rightleftarrows 2Me_3N{\cdot}Ga(CH_2CMe_3)_2PPh_2$$

The ^{31}P NMR spectrum of a mixture of $[(Me_3CCH_2)_2GaPPh_2]_2$ and NMe_3 in a 1:10 mole ratio, respectively, in benzene solution had resonances at -25.1 ppm ($[(Me_3CCH_2)_2GaPPh_2]_2$) and -43.7 ppm with relative intensities of 4.21 and 1.00, respectively. The resonance at -43.7 ppm might be due to the adduct $Me_3N{\cdot}Ga(CH_2CMe_3)_2PPh_2$. Previously, the compounds $(Me_3CCH_2)_2InPPh_2$, $(Me_3SiCH_2)_2InPPh_2$, and $(Me_3SiCH_2)_2GaPPh_2$ had been observed by ^{31}P NMR spectra to form apparently similar adducts with NMe_3.[6]

Acknowledgment. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positions, and additional C-C bond lengths and angles for $[(Me_3CCH_2)_2GaPPh_2]_2$ and $[(Me_3CCH_2)_2InPPh_2]_3$ (9 pages); listings of F_o and F_c for the two compounds (37 pages). Ordering information is given on any current masthead page.