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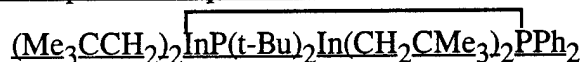
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TECHNICAL REPORT NO. 43

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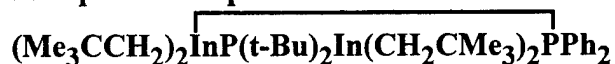
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Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, NY 14260

**Synthesis, Characterization and X-Ray Structural Study of a Dinuclear
Organoindium Phosphide Complex with Two Different Phosphide Moieties**



by

O. T. Beachley, Jr.* , Sun-Hua Leonard Chao, Melvyn Rowen Churchill* and Charles H. Lake

Abstract

An organoindium phosphide which incorporates two phosphido moieties in the same molecule $(\text{Me}_3\text{CCH}_2)_2\overline{\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$, **1**, has been synthesized in good yield from $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ in pentane solution and fully characterized. The compound exists as a single compound in the solid state according to an X-ray structural study but is in equilibrium with the starting compounds in benzene solution according to ^1H and ^{31}P NMR spectral data.

Organoindium phosphide dimers with four-membered rings provide interesting challenges for the syntheses of isomers as well as of compounds which have different substituents on the two phosphorus atoms, i.e. $R_2\overline{\text{InPR}_2}\overline{\text{InR}_2\text{PR}_2}$ or on the two indium atoms, i.e., $R_2\overline{\text{InPR}_2\text{InR}_2}\overline{\text{PR}_2}$. To our knowledge, there is only one example of an indium-phosphorus dimer with either the two phosphorus atoms or the two indium atoms with different substituents¹, $[(\text{Me}_3\text{CCH}_2)_2\overline{\text{InP}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{CMe}_3)_2}\overline{\text{P}(\text{H})(\text{SiMe}_3)}]$. This compound was apparently formed serendipitously as a minor product (ca. ~2% yield) from a reaction mixture of $(\text{Me}_3\text{CCH}_2)_2\text{InCl}$ and $\text{P}(\text{SiMe}_3)_3$ in a 1:1 mol ratio. The compound was reported to be unstable at room temperature under an inert atmosphere or upon standing in hydrocarbon solution. The products of decomposition were not described. In this paper, the synthesis and complete characterization of an organoindium phosphide dimer with different substituents on each of the two phosphorus atoms is described. The compound $(\text{Me}_3\text{CCH}_2)_2\overline{\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2}\overline{\text{PPh}_2}$, **1**, was synthesized by refluxing a pentane solution of $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2$ ² and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ ^{3,4} in equimolar quantities for 18 hours and was isolated by recrystallization. Characterization data for the product include C, H analysis, physical properties, ¹H and ³¹P NMR spectra and an X-ray structural study.

An X-ray structural study of **1** (Figure 1) confirms the presence of two different PR_2 ($\text{R} = \text{t-Bu, Ph}$) moieties in the same organoindium phosphide molecule. The unit cell consists of two molecules of **1** with puckered In-P-In-P rings. Selected interatomic distances and angles within the molecule are listed in Table 1 and 2.

The In_2P_2 core of **1** consists of a puckered ring with a fold angle of 12.2° about $\text{In}(1)\cdots\text{In}(2)$ axis (as defined by the dihedral angle between $\text{In}(1)\text{-P}(3)\text{-In}(2)$ and $\text{In}(1)\text{-P}(4)\text{-In}(2)$ planes) and a fold angle of 10.7° about the $\text{P}(3)\cdots\text{P}(4)$ axis. The compound $(\text{Me}_3\text{CCH}_2)_2\overline{\text{InP}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{CMe}_3)_2}\overline{\text{P}(\text{H})(\text{SiMe}_3)}$ ¹ is the only other organoindium phosphide which has a puckered In_2P_2 ring; this has a much larger fold angle (24.7°) across the $\text{In}\cdots\text{In}$ vector. The P-In-P angles for **1** average 82.5° and are slightly smaller than 83.4° found in $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ², while the In-P-In bond angles average 97.0° and are slightly larger than the $96.6(1)^\circ$ found for $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ². The average In-P bond distance for the $\text{P}(\text{t-Bu})_2$ moiety is 2.682 \AA and is slightly shorter than the average In-P distances of 2.698 \AA

for the PPh₂ moiety. (There is, however, some overlap and no clean separation into inequivalent sets.) The In-P(t-Bu)₂ distances in **1** are shorter than those in [(Me₃CCH₂)₂InP(t-Bu)₂]₂ (2.690-2.712 Å, average 2.701 Å).

The P(t-Bu)₂ moiety of **1** is associated with the bond lengths P(3)-C(51) = 1.897 (4) Å and P(3)-C(61) = 1.898 (5) Å (average = 1.898 Å). These bond lengths are similar to values of 1.891-1.895 Å for [(Me₃CCH₂)₂InP(t-Bu)₂]₂.² The plane C(51)-P(3)-C(61) makes an angle of 91.5 ° with the In(1)-P(3)-In(2) plane.

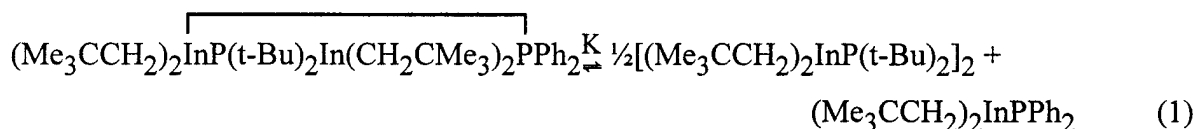
The PPh₂ moiety of **1** is associated with the bond lengths P(4)-C(71) = 1.833 (4) Å and P(4)-C(81) = 1.830 (5) Å (average = 1.832 Å). The P-C bond length is shorter than that in [(Me₃CCH₂)₂InPPh₂]₃ (average 1.845 Å),⁴ due, most probably, to the change from a trimeric to a dimeric molecule. The angle between the C(71)-P(4)-C(81) and In(1)-P(4)-In(2) planes is 75.3 °; these planes are clearly not perpendicular to each other. The two phenyl groups are twisted away from each other with a dihedral angle of 64.5 ° between the C(71)-C(76) and C(81)-C(86) planes. Note that overall the P-C bond lengths in the P(t-Bu)₂ moiety are substantially and significantly longer than those in the PPh₂ moiety (1.898 Å vs. 1.832 Å for the present, dissymmetric molecule).

The In-C bond lengths within the In(CH₂CMe₃)₂ systems average 2.191 Å and may be compared with those in [(Me₃CCH₂)₂InP(t-Bu)₂]₂ (average 2.213 Å)² or in [(Me₃CCH₂)₂InPPh₂]₃ (average 2.196 Å).⁴ The inter-ligand angles are C(11)-In(1)-C(21) = 121.5 (2) ° and C(31)-In(2)-C(41) = 130.5 (2) ° (average 126.0 °) and are much larger than those found in [(Me₃CCH₂)₂InP(t-Bu)₂]₂ (average 115.2 °).² The change in C-In-C angles is likely the result of a reduction from four bulky tert-butyl groups in [(Me₃CCH₂)₂InP(t-Bu)₂]₂² to only two in the present dissymmetric molecule. Dihedral angles are 83.2 ° between the C(11)-In(1)-C(21) and P(3)-In(1)-P(4) planes, and 89.3 ° between the C(31)-In(2)-C(41) and P(3)-In(2)-P(4) planes.

The physical properties of **1** are unique when compared with those of the symmetrical indium phosphides from which it was prepared. As the properties are compared, it should be noted that (Me₃CCH₂)₂InP(t-Bu)₂² is a dimer in the solid state and in benzene solution according to NMR studies. The solubility of [(Me₃CCH₂)₂InP(t-Bu)₂]₂ in benzene was

insufficient for a cryoscopic molecular study. In contrast, $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ ⁴ exists as a trimer in the solid state and as a monomer-dimer equilibrium mixture in benzene solution. Compound **1** decomposes at 171-173 °C. Both starting compounds also decompose rather than melt. The decomposition temperature of $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ² is 200-203 °C whereas $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ ⁴ is 143-150 °C. The solubility of the new mixed-bridge compound is much higher than of either starting material.

Even though **1** exists as a single compound in the solid state, an equilibrium mixture of species as represented by the following equation is present in benzene solution. The chemical shifts of all observed ³¹P and ¹H NMR resonances are assigned in Table 3. The three species are



readily identified in the ³¹P NMR spectrum. It is noteworthy that the equilibrium concentration of $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ is so small that the dimer is not observed. The ¹H NMR spectrum of **1** in benzene also confirms the presence of the equilibrium mixture of species. The equilibrium constant for Equation 1 calculated from integration data has a value of 0.2 ± 0.1 . The difference in splitting pattern is due to either the loss of symmetry in the In-P-In-P core when the four-membered ring becomes puckered, or more likely to the dissymmetry introduced by the two different substituents on phosphorus which precludes the possibility of "trans coupling". "Trans coupling" was observed for $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ². The proton signal for the methyl groups of the neopentyl groups attached to indium atoms is 1.21 ppm, which is between the corresponding signals for $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ (1.39 ppm)² and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ (1.06 ppm).^{3,4} The chemical shift for the methylene protons of neopentyl ligands in **1** is 1.54 ppm, which is the same as that observed for $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ² but is different than the chemical shift of the corresponding proton for $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ (1.43 ppm).^{3,4} The presence of only one set of proton resonances for the neopentyl protons in **1** indicates all the neopentyl ligands are magnetically equivalent in solution. This equivalence could be due to either a rapid inversion of the In₂P₂ ring on the NMR time scale, or the rapid breaking of the ring and rotation

of groups. In contrast, it should be noted that the exchange between **1** and its symmetrical derivatives $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ is slow on the NMR time scale as all three species are observed in benzene solution at the normal operating temperature of the spectrometer.

EXPERIMENTAL

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting materials $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ ² and $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ ^{3,4} were prepared by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. The ¹H spectra were recorded at 400 MHz by using a Varian VXR-400 spectrometer. Proton chemical shifts were reported in δ units (ppm) and were referenced to SiMe₄ at 0.00 ppm and C₆D₆ at 7.15 ppm. The ³¹P NMR spectra were recorded at 161.9 MHz on a Varian VXR-400 spectrometer. All phosphorus chemical shifts were referenced to 85% H₃PO₄ at 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectrum of Nujol mull between CsI plates was recorded with a Perkin-Elmer 683 spectrometer. Melting points were observed in sealed capillaries.

Synthesis of $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$, **1.** A small tube with a Solv-Seal joint was charged in the glove box with stoichiometric amounts of $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2$ (0.184 g, 0.458 mmol) and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ (0.203 g, 0.459 mmol). The assembled apparatus was then degassed and pentane (50 mL) was added by vacuum distillation. The resulting solution was heated by an oil bath at 60-75 °C for 18 h. The solution was then concentrated to about saturation by removing part of pentane by vacuum distillation. Recrystallization by slowly lowering temperature to -30 °C produced X-ray quality crystals of **1**, 0.254 g, 0.301 mmol, 65.7% yield based on $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2$. mp 170.9-172.9 °C (decomp.) Anal. Calcd., C, 56.88, H, 8.59. Found C, 56.74; H, 8.71. IR (Nujol mull) cm⁻¹, 3073 (w), 3060 (m), 2730 (vw), 2706 (vw), 2280 (vw), 1957 (vw), 1944 (w), 1886 (vw), 1872 (vw), 1809 (vw), 1580 (m), 1563 (w), 1431 (w), 1357 (s), 1298 (vw), 1275 (vw), 1232 (s, sh), 1169

(m, sh), 1116 (m), 1103 (m), 1095 (m), 1063 (w), 1022 (m), 1010 (m), 999 (m), 929 (w, sh), 904 (vw), 809 (w), 739 (vs), 731 (vs), 717 (vw), 688 (s), 562 (m), 504 (m), 472 (m), 447 (w), 430 (w), 375 (w).

X-ray Data Collection, Structure Determination and Refinement for 1. A colorless transparent single crystal (dimensions $0.23 \times 0.20 \times 0.20$ mm) was sealed under an argon atmosphere in a dry-box, with extremely strict anaerobic and moisture-free conditions into a thin-walled glass capillary. The crystal was then accurately centered in a eucentric goniometer on a Siemens R3m/V automated four-circle diffractometer. Determination of unit cell dimensions and data collection (Mo $K\alpha$ radiation, $\lambda = 0.710730$ Å) were carried out as has been described in detail previously.⁵ Details are provided in Table 4.

The crystal belongs to the triclinic crystal system. Possible space groups are the noncentrosymmetric $P1$ (C_1^1 ; No. 1) or the centrosymmetric $P\bar{1}$ (C_1^1 ; No. 2). Intensity statistics, frequency of occurrence data⁶ and the probability of a synthetic material from achiral precursors being itself achiral⁷ all militate in favor of the centrosymmetric possibility, $P\bar{1}$. This space group was assumed and was confirmed by the successful solution of the structural analysis.

Crystallographic calculations were carried out on a VAXstation 3100 computer system with use of the Siemens SHELXTL PLUS program package (Release 4.11, VMS).^{8,9}

The analytical scattering factors for neutral atoms were corrected explicitly for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.¹⁰ The structure was solved by a combination of direct methods, difference-Fourier syntheses and least-squares refinement. All non-hydrogen atoms were located and hydrogen atoms were included in their appropriate idealized staggered tetrahedral or trigonal positions with $d(\text{C-H})$ set at 0.96 Å.¹¹

Convergence was reached with $R = 4.53\%$ and $R_w = 3.78\%$ for all 5787 unique reflections and $R = 2.54\%$ and $R_w = 2.70\%$ for those 4162 reflections with $|F_o| > 6\sigma(|F_o|)$.

Acknowledgments

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Supporting Information Available

Complete tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters and calculated positions for hydrogen atoms (6 pages). Ordering information is given on any current masthead page.

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Table 1. Selected Distances for $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$.

(A) Indium-Phosphorus Distances

In(1)-P(3)	2.674(1)	In(2)-P(3)	2.689(1)
In(1)-P(4)	2.685(1)	In(2)-P(4)	2.710(1)

(B) Indium-Carbon Distances

In(1)-C(11)	2.193(5)	In(2)-C(31)	2.197(4)
In(1)-C(21)	2.174(5)	In(2)-C(41)	2.200(4)

(C) Phosphorus-Carbon Distances

P(3)-C(51)	1.897(4)	P(4)-C(71)	1.833(4)
P(3)-C(61)	1.898(5)	P(4)-C(81)	1.830(5)

(D) Cross ring contacts

In(1)•••In(2)	4.028	P(3)•••P(4)	3.631
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Table 2. Selected Angles (deg) for $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$.

(A) Angles around Indium Atoms

P(3)-In(1)-P(4)	82.8(1)	P(3)-In(2)-P(4)	82.1(1)
P(3)-In(1)-C(11)	106.3(2)	P(3)-In(2)-C(31)	114.8(1)
P(3)-In(1)-C(21)	114.8(2)	P(3)-In(2)-C(41)	107.6(1)
P(4)-In(1)-C(11)	98.6(1)	P(4)-In(2)-C(31)	108.2(1)
P(4)-In(1)-C(21)	125.4(1)	P(4)-In(2)-C(41)	101.7(1)
C(11)-In(1)-C(21)	121.5(2)	C(31)-In(2)-C(41)	130.5(2)

(B) Angles around Phosphorus Atoms

In(1)-P(3)-In(2)	97.4(1)	In(1)-P(4)-In(2)	96.6(1)
In(1)-P(3)-C(51)	111.6(2)	In(1)-P(4)-C(71)	126.9(1)
In(1)-P(3)-C(61)	110.4(1)	In(1)-P(4)-C(81)	102.5(1)
In(2)-P(3)-C(51)	116.2(1)	In(2)-P(4)-C(71)	107.5(1)
In(2)-P(3)-C(61)	110.8(1)	In(2)-P(4)-C(81)	121.1(1)
C(51)-P(3)-C(61)	109.9(2)	C(71)-P(4)-C(81)	103.9(2)

(C) Selected Angles around Carbon Atoms

In(1)-C(11)-C(12)	126.7(4)	In(2)-C(31)-C(32)	122.2(3)
In(1)-C(21)-C(22)	126.5(4)	In(2)-C(41)-C(42)	122.5(3)
P(3)-C(51)-C(52)	113.6(3)	P(3)-C(51)-C(53)	106.1(3)
P(3)-C(51)-C(54)	111.0(3)	P(3)-C(61)-C(62)	113.1(3)
P(3)-C(61)-C(63)	105.6(3)	P(3)-C(61)-C(64)	111.8(3)
P(4)-C(71)-C(72)	121.5(3)	P(4)-C(71)-C(76)	120.6(3)
P(4)-C(81)-C(82)	121.4(4)	P(4)-C(81)-C(86)	120.3(3)

Table 3. ^1H and ^{31}P NMR Resonances for $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$, and for Solutions of $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$ and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ (ppm) in Benzene- d_6 .

	$(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$	$[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2^2$	$(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2^{3,4}$
$^1\text{H InCCCH}_3$	1.07 (s)*		1.06 (s)
	1.21 (s)		
	1.39 (s)**	1.39 (s)	
PCCH_3	1.43 (d, J = 13 Hz)		
	1.46 (t, J = 7 Hz)**	1.46 (t, J = 7 Hz)	
InCH_2	1.54 (br)	1.54 (s)	
PPh	6.96 (td)		
	7.09 (td)		
	7.70 (dd)		
$^{31}\text{P}\{^1\text{H}\}$			
			-49.7 (s, dimer)
	-28.5 (s)*		-30.2 (s, monomer)
	-25.6 (d, J = 360 Hz)		
	46.7 (d, J = 359 Hz)		
	56.3 (s)**	55.0 (s)	

* Resonances due to $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$

** Resonances due to $[(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2]_2$

Table 4. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$.

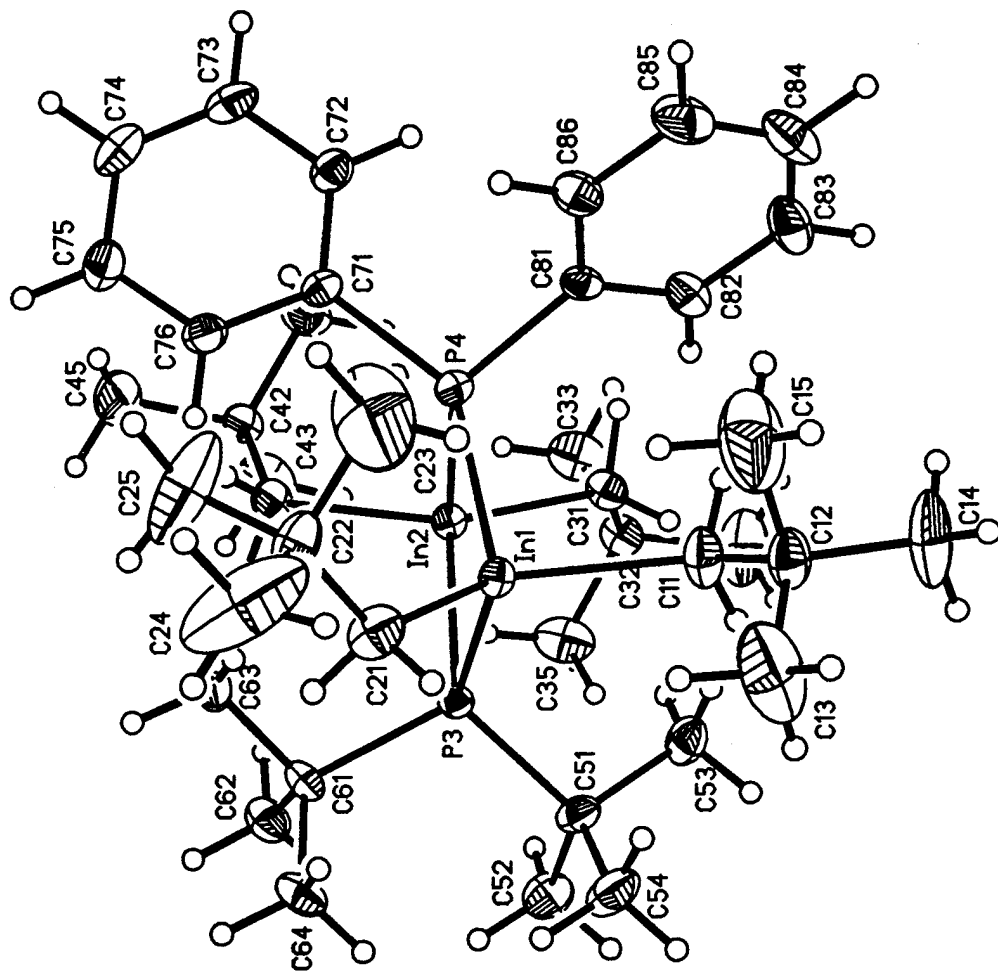
molecular formula	$\text{C}_{40}\text{H}_{72}\text{In}_2\text{P}_2$
crystal system	triclinic
space group	$\bar{P}1$ (No. 2)
temp., °C (K)	22 (295)
a, Å	9.9191 (12)
b, Å	12.1506 (15)
c, Å	18.7589 (25)
α , deg.	97.974 (10)
β , deg.	100.448 (10)
γ , deg.	90.052 (10)
V, Å ³	2201.3 (5)
Z	2
formula weight	844.6
D, g/cm ³	1.274
μ , mm ⁻¹	1.126
2 θ range, deg	5.0 - 45.0 °
index ranges	h 0 → 10
	k -13 → 13
	l -20 → 19

Table 4. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$ (Cont).

no. of reflections collect	6278
no. of unique reflections	5787
no. of reflections $> 6\sigma$	4162
weighting scheme	$1/[\sigma^2(\text{F}) + 0.0005\text{F}^2]$
no. parameters refined	398
goodness-of-fit	1.04
largest and mean Δ/σ	0.002, 0.000
data-to-parameter ratio	14.5:1
R indices (all data)	$\text{R} = 4.53\%$, $\text{R}_w = 3.78\%$
R indices (6σ data)	$\text{R} = 2.54\%$, $\text{R}_w = 2.70\%$
largest diff. peak, $\text{e}^-/\text{\AA}^3$	0.61
deepest diff. hole, $\text{e}^-/\text{\AA}^3$	-0.44

Figure Captions

Figure 1. Labeling of atoms in the $(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{t-Bu})_2\text{In}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$ molecule. Note the slight puckering of the four-membered In_2P_2 ring [ORTEP-II diagram; 30% probability ellipsoids.]



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