ORGANOMETALLICS

Synthesis and characterization of trimethylsilyl phosphide derivatives of dineopentylindium chloride. X-ray crystal structures of [Me(Me3CCH2)InP)(SiMe3)2]2, [cyclic] (Me3CCH2)2InP(SiMe3)2In(CH2CMe3)2Cl, and [cyclic] (Me3CCH2)2InP(SiMe3)2In(CH2CMe3)2PH(SiMe3)

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Organometallics, **1993**, 12 (8), 3363-3367• DOI: 10.1021/om00032a069 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Synthesis and Characterization of Trimethylsilyl Phosphide Derivatives of Dineopentylindium Chloride. X-ray Crystal Structures of $[Me(Me_3CCH_2)InP(SiMe_3)_2]_2$, $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$, and $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)$

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Received March 17, 1993

Summary: Three new neopentylindium compounds, $[Me(Me_3CCH_2)InP(SiMe_3)_2]_2$ *(1),* $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$ *(2), and* $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)$ *(3), are reported. Dimer 1 contains two different exocyclic alkyl ligands on the group 13 center and is the only product isolated from the reaction of* $(Me_3CCH_2)_2InCl$ *and* $LiP(SiMe_3)_2$ *in either a 1:1 or 2:1 mole ratio. Compound 1 crystallizes in a trans configuration in the monoclinic space group* $P2_1/c$*, with unit cell parameters* $a = 11.581(1)$ Å, $b = 10.284(1)$ Å, $c = 18.221(2)$ Å, $\beta = 111.51(1)°$*, and* $V = 1225.6(7)$ Å^3 *for* $Z = 2$*. Compound 2 is the major product isolated from the reaction of* $(Me_3CCH_2)_2InCl$ *and* $P(SiMe_3)_3$ *in either a 1:1 or 2:1 mole ratio and is an example of an In–P–In–Cl-ring-containing compound. Crystals of 2 belong to the monoclinic system, space group C2/c, with unit cell parameters* $a = 20.242(2)$ Å, $b = 9.883(1)$ Å, $c = 19.709(2)$ Å, $\beta = 99.71(1)°$*, and* $V = 3886(1)$ Å^3 *for* $Z = 4$*. Compound 3, isolated as a minor component (ca. ~2%) from the reaction of* $(Me_3CCH_2)_2InCl$ *and* $P(SiMe_3)_3$ *in a 1:1 mole ratio, is the first example of an indium compound containing an In–P–In–P core wherein the phosphorus centers are not symmetrically substituted. This compound crystallizes in the triclinic space group* $P\bar{1}$*, with unit cell parameters* $a = 12.426(1)$ Å, $b = 18.497(2)$ Å, $c = 10.156(1)$ Å, $\alpha = 94.49(1)°$, $\beta = 104.62(1)°$, $\gamma = 81.22(1)°$*, and* $V = 2230.3(7)$ Å^3 *for* $Z = 2$*.*

The use of LiCl elimination and dehalosilylation reactions to form bonds between group 13 and group 15 elements has been widely employed over the past several years.[1–4] These reactions have produced a number of new compounds, many of which are dimeric species of the formula $[R_2ME(SiMe_3)_2]_2$ (M = Al, E = As, R = Me,[5] Et,[6] $Me_2C(H)CH_2$;[5] M = Al, E = P, R = Et;[7] M = Ga, E = As, R = Ph,[8,9] Me_3SiCH_2,[10] Me_3CCH_2;[11] M = Ga, E = P, R = Cl;[12] M = In, E = As,[13] P,[2,14] R = Ph, Me_3SiCH_2). Moreover, this approach has led to the discovery of "mixed-bridge" species of the general formula $R_2ME(SiMe_3)_2MR_2(Cl)$ (M = Ga, E = As, R = Ph,[8,9] Me_3SiCH_2,[10] Me_3CCH_2;[11] M = Ga, E = P, R = Ph;[15] M = In, E = As,[13] P,[14] R = Me_3SiCH_2). Additionally, species such as $[R(R')ME(SiMe_3)_2]_2$ (R = Ph, R′ = Me_3SiCH_2, E = As, M = In; R = Me, E = As, P, M = In; R = Cl, E = P, M = In) have been isolated.[16] Herein, we report the synthesis, characterization [partial elemental analyses (C, H), mp, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra], and solid-state structures of $[Me(Me_3CCH_2)In\text{-}P(SiMe_3)_2]_2$ (1), a dimeric compound containing two different exocyclic alkyl ligands on the group 13 center, $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (2), the second example of an In–P–In–Cl-ring-containing compound, and $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)$ (3), the first compound to contain an In–P–In–P core wherein the two phosphorus centers do not bear the same substitutents.

Experimental Section

General Considerations. All manipulations were performed using Schlenk, drybox, or high-vacuum techniques. Solvents (including those for NMR spectra) were appropriately dried and distilled under dinitrogen prior to use. Literature methods were used to prepare $(Me_3CCH_2)_2InCl$[17] and $P(SiMe_3)_3$.[18] $LiP(SiMe_3)_2$[19] was prepared *via* the 1:1 mole reaction of MeLi with $P(SiMe_3)_3$. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra (sealed 5-mm tubes) were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 121.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were

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0276-7333/93/2312-3363$04.00/0

referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra were referenced externally to $\mathrm{H_3PO_4}$ at δ 0.00 ppm. Melting points (uncorrected) were obtained on a Thomas-Hoover Uni-melt apparatus in sealed capillaries. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of $[\mathrm{Me(Me_3CCH_2)InP(SiMe_3)_2}]_2$ (1). Method a. Reaction of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{LiP(SiMe_3)_2}$ in a 1:1 Mole Ratio. A one-necked 200-mL round-bottomed flask equipped with a Teflon valve and a micro-stirbar was charged with 0.500 g (1.62 mmol) of $\mathrm{(Me_3CCH_2)_2InCl}$ dissolved in 25 mL of hexane. $\mathrm{LiP(SiMe_3)_2}$ (0.299 g, 1.62 mmol) in 45 mL of hexane was then added, and the turbid solution was stirred at room temperature for 24 h. The volatiles were removed *in vacuo* from the resulting light yellow solution, leaving a pale yellow amorphous solid. Dissolution of the solid in ~5 mL of pentane and storage at −15 °C for 2 days yielded colorless crystals of 1 suitable for X-ray analysis [0.386 g, 63% yield based on $\mathrm{(Me_3CCH_2)_2InCl}$]; mp 185 °C (yellows), 200–214 °C dec with melt. Anal. Calcd (Found) for $\mathrm{C_{24}H_{64}In_2P_2Si_4}$: C, 38.10 (38.28); H, 8.52 (8.34). ^{1}H NMR: δ 0.39 (t, 18 H, *cis*-SiCH_3, $J_{\mathrm{P-H}}$ = 2.60 Hz), 0.24 (t, 36 H, *trans*-SiCH_3, $J_{\mathrm{P-H}}$ = 2.50), 0.45 (t, 18 H, *cis*-SiCH_3, $J_{\mathrm{P-H}}$ = 2.60), 1.05 (s, 4 H, *trans*-CH_2), 1.09 (s, 4 H, *cis*-CH_2), 1.157 (bs, 36 H, *cis*- and *trans*-CCH_3), 1.20 (s, 4 H, *trans*-CH_2), 1.23 (s, 4 H, *cis*-CH_2). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 4.56–5.43 (complex mult, *cis*- and *trans*-SiCH$_3$), 32.82 (s, *cis*-CH$_2$), 33.12 (s, *trans*-CH$_2$), 34.40 (s, *cis*-CH$_3$), 34.65 (s, *trans*-CH$_3$), 34.92 (s, *trans*-CCH$_3$), 35.20 (s, *cis*-CCH$_3$), 43.83 (s, *cis*-C), 44.10 (s, *trans*-C). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −239.56 (s, *cis*), −239.42 (s, *trans*).

Method b. Reaction of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{LiP(SiMe_3)_2}$ in a 2:1 Mole Ratio. In an arrangement identical to that described above, 0.500 g (1.62 mmol) of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{LiP(SiMe_3)_2}$ (0.150 g, 0.810 mmol) were combined. After the resulting solution was stirred for 48 h, volatiles were removed *in vacuo*, affording a pale yellow oil which was dissolved in ~5 mL of pentane. After 2 days, crystals of 1 (authenticated *via* mp, ^{1}H NMR, and X-ray diffraction data) formed in a 42% yield [0.256 g, based on $\mathrm{(Me_3CCH_2)_2InCl}$]. Additionally, the ^{1}H NMR spectrum of the remaining oily material confirmed the presence of unreacted $\mathrm{(Me_3CCH_2)_2InCl}$.

Synthesis of $\mathrm{(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl}$ (2). Method a. Reaction of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{P(SiMe_3)_3}$ in a 2:1 Mole Ratio. A one-necked 200-mL round-bottomed flask equipped with a Teflon valve and a micro-stirbar was charged with 0.276 g (0.895 mmol) of $\mathrm{(Me_3CCH_2)_2InCl}$ dissolved in 25 mL of hexane. $\mathrm{P(SiMe_3)_3}$ (0.112 g, 0.447 mmol) in 25 mL of hexane was then added, and the clear solution was stirred at room temperature for 24 h. Removal of the volatiles from the resulting light yellow solution *in vacuo* left a pale yellow amorphous solid which was dissolved in ~5 mL of pentane and stored at −15 °C for 5 days, after which colorless crystals of 2 suitable for X-ray analysis were obtained [0.195 g, 60% yield based on $\mathrm{(Me_3CCH_2)_2InCl}$]; mp 95–104 °C with dec. Anal. Calcd (Found) for $\mathrm{C_{26}H_{62}ClIn_2PSi_2}$: C, 42.95 (42.37); H, 8.60 (7.95); Cl, 4.88 (5.21). ^{1}H NMR: δ 0.39 (d, 18 H, SiCH_3, $J_{\mathrm{P-H}}$ = 5.13 Hz), 1.17 (s, 8 H, CH_2), 1.25 (s, 36 H, CCH_3). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 5.00 (d, SiCH$_3$, $J_{\mathrm{P-C}}$ = 8.4 Hz), 33.27 (bs, CH$_2$), 35.06 (s, CH$_3$), 43.62 (s, C). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −227.34.

Method b. Reaction of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{P(SiMe_3)_3}$ in a 1:1 Mole Ratio. In an arrangement identical to that described above for the 2:1 mole ratio reaction, 0.276 g (0.894 mmol) of $\mathrm{(Me_3CCH_2)_2InCl}$ and $\mathrm{P(SiMe_3)_3}$ (0.224 g, 0.894 mmol) were combined. After the resulting solution was stirred for 48 h, removal of the volatiles *in vacuo* afforded a viscous yellow oil which was dissolved in ~5 mL of pentane. After 4 days crystals of 2 (identified *via* mp, ^{1}H NMR, and X-ray diffraction data) formed in a 36% yield [0.117 g, based on $\mathrm{(Me_3CCH_2)_2InCl}$]. Additionally, the ^{1}H NMR spectrum of the remaining oily material confirmed the presence of unreacted $\mathrm{P(SiMe_3)_3}$.

Isolation of $\mathrm{(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)}$ (3). When the oil remaining from the above 1:1 mole ratio reaction leading to the formation of 2 was allowed to stand in a refrigerator for several days, a few small pale yellow crystals grew along the sides of the flask. X-ray crystallographic analysis (*vide infra*) established the identity of this crystalline product as 3. Unfortunately, due to subsequent decomposition of this material, no elemental analysis data could be obtained; mp 104–109 °C. ^{1}H NMR: δ 0.33 (d, 9 H, SiCH_3, $J_{\mathrm{P-H}}$ = 3.37 Hz), 0.45 (s, 18 H, SiCH_3, $J_{\mathrm{P-H}}$ = 4.81 Hz), 1.18 (bs, 8 H, CH_2), 1.26 (s, 18 H, CH_3), 1.27 (s, 18 H, CH_3), 1.46–1.54 (bs, PH). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: δ 3.67 (d, HPSiCH$_3$, $J_{\mathrm{P-C}}$ = 7.5 Hz), 5.30 (d, PSiCH$_3$, $J_{\mathrm{P-C}}$ = 7.9 Hz), 34.81 (bs, CH$_2$), 35.15 (s, CH$_3$), 35.22 (s, CH$_3$), 43.50 (bs, C), 43.67 (bs, C). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ −210.86 (s, HPSiMe$_3$), −208.97 [s, P(SiMe$_3$)$_2$]. ^{31}P NMR: δ −211.87 to −207.97 (d, HPSiMe$_3$, $J_{\mathrm{P-H}}$ = 473 Hz), −209.12 [s, P(SiMe$_3$)$_2$].

X-ray Crystallographic Measurements for 1–3. Crystals of each compound were flame-sealed inside thin-walled 6-mm glass capillaries under an argon atmosphere. All measurements were performed on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Cu Kα radiation, λ = 1.5418 Å; Crystal Structure Center, Duke University). Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 25 reflections ($35° < \theta < 40°$ for 1, $30° < \theta < 35°$ for 2, $36° < \theta < 40°$ for 3) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects. Empirical absorption corrections, based on the φ dependency of the intensities of several reflections with χ *ca.* 90°, were also applied. The intensities of four reference reflections, remeasured every 2 h throughout the data collections, indicated that significant deterioration of 1 and 3 had occurred; accordingly, linear decay corrections were applied to the data recorded from these crystals. From totals of 3600, 3302, and 9186 nonequivalent measurements for 1–3, respectively, those 1825, 1175, and 5043 reflections with $I > 3.0\sigma(I)$ were retained for the structure analyses. The monoclinic space group $P2_1/c$ for 1 was defined uniquely by the Laue symmetry and systematic absences, $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$. For 2, Laue symmetry and systematic absences (hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$) were compatible with the monoclinic space groups Cc and $C2/c$; the latter was assumed at the outset of the analysis and was confirmed by the successful solution and refinement. In the case of 3, Laue symmetry indicated that the space group was either $P1$ or $P\bar{1}$; the centrosymmetric choice was assumed initially and was confirmed by the structure analysis and refinement.

Solution and Refinement of 1–3. The crystal structures of 1–3 were solved by the heavy-atom approach. With only two formula units in the unit cell of space group $P2_1/c$, dimer 1 is required to lie on a crystallographic center of symmetry. For 2, the presence of only four molecules in the unit cell of space group $C2/c$ demands that they lie on crystallographic C_2 symmetry axes. In triclinic crystals of 3 the molecules lie in general positions. Approximate coordinates for the In atoms for all three compounds were derived from Patterson maps, and the remaining non-hydrogen atoms were located by Fourier techniques. In the case of 3, the electron density distributions revealed that the methyl carbon atoms of one of the neopentyl groups was disordered over two orientations with ca. 50% occupancy of each. Several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and isotropic thermal parameters for each compound were followed by refinement of positional and anisotropic thermal parameters (except for the carbon atoms of the disordered neopentyl group in 3 where they were constrained to be isotropic). Hydrogen atoms, other than those associated with the ill-defined neopentyl groups in 2 and the disordered neopentyl group in 3, were incorporated at their calculated positions [C(sp^3)–H = 1.05 Å] in the later cycles. An extinction correction was included as a variable in the final iterations for 2 and 3. Parameter refinement converged at R = 0.052 (R_w = 0.064, GOF = 1.37) for 1, R = 0.069 (R_w = 0.094, GOF = 1.91) for 2, and R = 0.057 (R_w = 0.075, GOF = 1.65) for 3. Final difference Fourier syntheses contained no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion correc-

Table I. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq} (Å^2)
In	0.13863(6)	0.07623(6)	0.08356(4)	4.28(1)
P	–0.1045(2)	0.0757(2)	0.0396(1)	3.95(5)
Si(1)	–0.1846(3)	0.2777(3)	0.0163(2)	4.67(7)
Si(2)	–0.1775(2)	–0.0231(3)	0.1244(2)	4.68(7)
C(1)	0.228(1)	–0.017(1)	0.1973(7)	6.4(3)
C(2)	0.363(1)	0.020(1)	0.2453(6)	5.3(3)
C(3)	0.415(1)	–0.069(2)	0.3182(8)	9.0(4)
C(4)	0.442(1)	–0.001(2)	0.1963(9)	11.6(5)
C(5)	0.367(2)	0.157(1)	0.2722(9)	11.1(6)
C(6)	0.198(1)	0.268(1)	0.0618(7)	6.4(3)
C(11)	–0.157(1)	0.344(1)	–0.0714(6)	7.0(3)
C(12)	–0.353(1)	0.277(1)	–0.0040(7)	6.6(3)
C(13)	–0.103(1)	0.384(1)	0.1028(7)	6.8(4)
C(21)	–0.344(1)	–0.064(1)	0.0725(7)	6.8(3)
C(22)	–0.161(1)	0.078(1)	0.2113(7)	8.2(4)
C(23)	–0.088(1)	–0.175(1)	0.1592(6)	6.4(3)

Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Parameters for 2, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq} (Å^2)
In	0.0891(1)	0.2693(1)	0.2316(1)	8.73(3)
P	0.0000(–)[a]	0.0863(7)	0.2500(–)[a]	8.4(2)
Cl	0.0000(–)[a]	0.4431(8)	0.2500(–)[a]	23.7(5)
Si	0.0355(3)	–0.0501(6)	0.3409(3)	10.1(2)
C(1)	0.159(2)	0.296(3)	0.325(2)	30(1)
C(2)	0.211(1)	0.375(2)	0.344(1)	11(1)
C(3)	0.193(2)	0.516(3)	0.317(1)	23(1)
C(4)	0.231(2)	0.383(3)	0.423(1)	29(2)
C(5)	0.270(2)	0.357(5)	0.328(3)	37(2)
C(6)	0.099(2)	0.261(3)	0.128(2)	36(1)
C(7)	0.124(1)	0.345(2)	0.079(1)	13(1)
C(8)	0.080(2)	0.381(3)	0.013(1)	24(1)
C(9)	0.086(3)	0.478(6)	0.100(3)	44(3)
C(10)	0.181(1)	0.417(4)	0.100(2)	28(1)
C(11)	0.058(1)	0.057(3)	0.419(1)	13(1)
C(12)	0.107(1)	–0.151(3)	0.329(1)	18(1)
C(13)	–0.034(1)	–0.169(3)	0.356(1)	17(1)

[a] Fixed by symmetry.

Table III. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 3, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq} (Å^2)
In(1)	0.44288(4)	0.23244(3)	0.27665(5)	4.79(1)
In(2)	0.11643(4)	0.27668(3)	0.16434(6)	5.69(1)
P(1)	0.2910(2)	0.3362(1)	0.1418(2)	4.75(4)
P(2)	0.2674(2)	0.2029(1)	0.3560(2)	5.42(4)
Si(1)	0.2732(2)	0.3607(2)	–0.0770(3)	6.78(6)
Si(2)	0.3019(2)	0.4433(1)	0.2621(3)	6.48(6)
Si(3)	0.2602(3)	0.0940(2)	0.4349(3)	6.87(6)
C(11)	0.289(1)	0.2726(7)	–0.179(1)	8.1(3)
C(12)	0.127(1)	0.4093(8)	–0.148(1)	11.5(5)
C(13)	0.379(1)	0.4182(8)	–0.094(1)	11.6(3)
C(21)	0.293(1)	0.4273(6)	0.437(1)	8.3(3)
C(22)	0.184(1)	0.5149(6)	0.183(2)	10.0(4)
C(23)	0.438(1)	0.4772(5)	0.271(1)	8.5(3)
C(31)	0.120(1)	0.0879(9)	0.459(2)	13.7(5)
C(32)	0.291(2)	0.0207(6)	0.309(1)	12.5(5)
C(33)	0.361(1)	0.0825(8)	0.603(1)	13.2(5)
C(101)	0.568(1)	0.2850(5)	0.427(1)	5.6(2)
C(102)	0.614(1)	0.2582(5)	0.571(1)	6.0(2)
C(103)	0.711(1)	0.2995(7)	0.648(1)	9.8(4)
C(104)	0.524(1)	0.2697(11)	0.650(1)	12.7(6)
C(105)	0.660(1)	0.1770(7)	0.568(1)	10.0(4)
C(106)	0.481(1)	0.1427(5)	0.134(1)	6.6(2)
C(107)	0.591(1)	0.1371(6)	0.091(1)	6.7(2)
C(108)	0.608(1)	0.2110(8)	0.050(1)	9.0(3)
C(109)	0.689(1)	0.1124(8)	0.208(1)	9.9(4)
C(110)	0.592(1)	0.0816(10)	–0.026(1)	12.4(5)
C(201)	0.032(2)	0.2265(9)	–0.037(2)	18.0(6)
C(202)	0.034(1)	0.1473(6)	–0.064(1)	8.5(3)
C(203)	–0.029(1)	0.1223(8)	0.029(2)	19.4(5)
C(204)	0.151(2)	0.1242(14)	–0.023(2)	23.9(8)
C(205)	–0.003(2)	0.1162(14)	–0.191(2)	23.5(8)
C(206)	0.003(1)	0.3611(8)	0.246(2)	13.9(4)
C(207)	–0.078(1)	0.3441(6)	0.315(1)	8.6(3)
C(208)[a]	–0.185(3)	0.352(2)	0.182(4)	13.1(10)
C(209)[a]	–0.074(2)	0.268(1)	0.368(2)	7.8(5)
C(210)[a]	–0.132(2)	0.410(1)	0.404(2)	8.6(6)
C(208′)[a]	0.008(3)	0.335(2)	0.463(3)	12.5(10)
C(209′)[a]	–0.111(2)	0.267(1)	0.295(2)	7.3(5)
C(210′)[a]	–0.181(3)	0.403(2)	0.311(3)	12.4(10)

[a] These atoms were refined isotropically with occupancy factors = 0.50.

tions were taken from ref 20. In the least-squares iterations, $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP 3.0).[21] Non-hydrogen atom fractional coordinates for 1–3 are provided in Tables I–III, respectively.

Results and Discussion

The room temperature reaction of $(Me_3CCH_2)_2InCl$ with $LiP(SiMe_3)_2$ in either a 1:1 or 2:1 mole ratio results in the formation of $[Me(Me_3CCH_2)InP(SiMe_3)_2]_2$ (**1**) in 63% and 42% yields, respectively. The isolation of **1** from a 1:1 reaction designed to form $[(Me_3CCH_2)_2InP(SiMe_3)_2]_2$ (to date, attempts to form this dimer *via* LiCl elimination, dehalosilylation, or alkane elimination have been unsuccessful) as well as from the 2:1 reaction designed to form mixed-bridge **2** is surprising. To our knowledge, there are only four other examples of similar compounds in which the metal center is bonded to two different exocyclic organic groups, $[Me_3SiCH_2(Ph)InAs(SiMe_3)_2]_2$ (**4**),[16] $[Me_3SiCH_2(Me)InAs(SiMe_3)_2]_2$ (**5**),[16] $[Me_3SiCH_2(Me)InP(SiMe_3)_2]_2$ (**6**),[16] and $[Me_3SiCH_2(Me_3CCH_2)InPEt_2]_2$ (**7**).[22]

Compound **1** is a colorless crystalline solid which is extremely air-sensitive but stable at room temperature under an inert atmosphere. As was observed for its Me_3SiCH_2 analogs **4**–**6**,[16] **1** undergoes appreciable decomposition upon standing in hydrocarbon solution and its room temperature ^1H and ^{13}C NMR solution spectra clearly demonstrate the existence of both *cis* and *trans* isomers. The co-occurrence of both isomers is manifested in the ^1H NMR spectrum by a triplet for the *trans* related $SiMe_3$ group protons and two triplets for the *cis*-related groups due to virtual coupling with the ring phosphorus atoms. The ^{31}P NMR spectrum exhibits two sharp resonances corresponding to each of these isomers. It is noteworthy that no *cis* isomer has thus far been isolated in the solid state, suggesting that crystal packing interactions favor crystallization of the *trans* isomer.

Crystals of compound **1** belong to the centrosymmetric space group $P2_1/c$ and are isomorphous with those of the Me_3SiCH_2 analog **6**; accordingly, the $\overline{\mathrm{In{-}P{-}In{-}P}}$ core is planar. Figure 1 presents an ORTEP diagram of **1** showing the atom-numbering scheme. That the In–P bond lengths

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(20) *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(21) *Enraf-Nonius Structure Determination Package (SDP 3.0)*; Enraf-Nonius: Delft, The Netherlands, 1985.

(22) Beachley, O. T., Jr.; Maloney, J. D.; Churchill, M. R.; Lake, C. H. *Organometallics* **1991**, *10*, 3568.

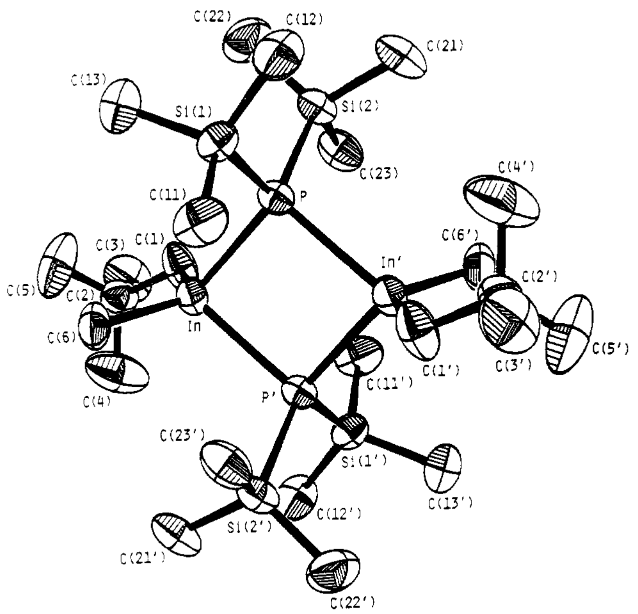

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of $[Me(Me_3CCH_2)InP(SiMe_3)_2]_2$ (**1**). Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): In–P = 2.630(2), In–P′ = 2.643(2), In–C(1) = 2.17(1), In–C(6) = 2.17(1), P–Si(1) = 2.251(4), P–Si(2) = 2.257(4); P–In–P′ = 86.0(1), C(1)–In–C(6) = 120.2(4), In–P–In′ = 94.0(1), Si(1)–P–Si(2) = 108.2(2).

of 2.630(2) and 2.643(2) Å in **1** lie close to those found in **6**[16] [2.632(2), 2.638(1) Å] is not unexpected given the similar nature of the substituents at In (Me_3CCH_2 in **1** and Me_3SiCH_2 in **6**). In contrast, the mean In–P bond length of 2.655 Å in $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (**8**)[14] is slightly longer than the corresponding means in **1** [2.637 Å] and **6** [2.635 Å] due to the increased steric compression accompanying the replacement of Me by Me_3SiCH_2. Endocyclic In–P–In and P–In–P bond angles of 94.0(1) and 86.0(1)°, respectively, in **1** are similar to those of 93.35(6)° and 86.65(5)°, respectively, in **6** as well as corresponding values of 93.6(1)° and a mean of 86.3° in **8**; moreover, they are in accord with the usually observed pattern, i.e. P–In–P ≪ In–P–In.[1,4,16] The Si–P–Si bond angle in **1** [108.2(2)°] is essentially the same as that in **6** [108.0(1)°] but slightly smaller than that in more sterically encumbered bis(trimethylsilyl) **8** [105.7(2)°]. The exocyclic bond angle subtended at the In atom in **1** [120.2(2)°] is slightly larger that of 118.3(2)° in **6**, reflecting the increased steric requirements of Me_3CCH_2 versus Me_3SiCH_2, and both angles are smaller than that of 122.7(4)° in **8**.

It has been demonstrated previously that **8** can be prepared readily *via* the dehalosilylation reaction of $(Me_3SiCH_2)_2InCl$ and $P(SiMe_3)_3$ in a 1:1 mole ratio whereas $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**9**), results from the 2:1 mole ratio reaction.[14] In contrast, the reaction of $(Me_3CCH_2)_2InCl$ and $P(SiMe_3)_3$ in either a 1:1 or 2:1 mole ratio leads to the formation of $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**2**) as the major product. In the case of the 1:1 mole reaction, the presence of unreacted $P(SiMe_3)_3$ in the reaction mixture was confirmed *via* ^1H NMR spectroscopy. Compound **2** is the second reported representative of a species containing an In–P–In–Cl core. Like the earlier example **1**, compound **2** is a colorless crystalline solid that is stable at room temperature under an inert atmosphere and decomposes upon standing in hydrocarbon solution. Room temperature solution NMR spectral data indicate that, similar to its Me_3SiCH_2 analog **9**, **2** does not appear to undergo any discernible isomerizations or equilibria, as only signals consistent with its solid-state structure are obtained.

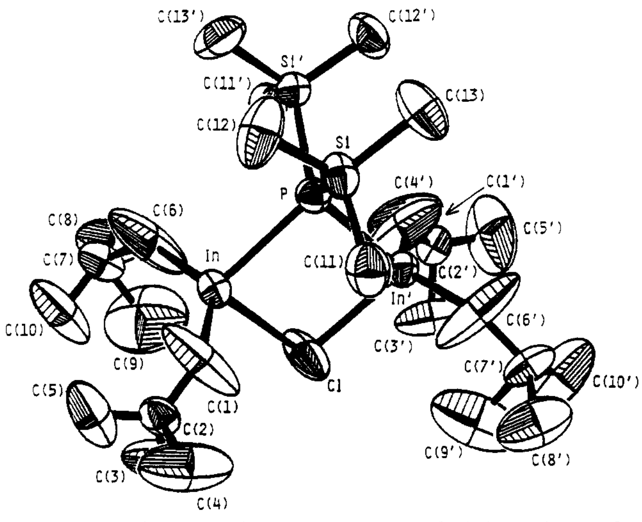

Figure 2. ORTEP diagram (20% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2Cl$ (**2**). Primed atoms are related to the unprimed atoms by a crystallographic C_2 axis of symmetry passing through the P and Cl atoms. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): In–P = 2.622(5), In–Cl = 2.560(7), In–C(1) = 2.14(4), In–C(6) = 2.09(4), P–Si = 2.260(7); P–In–Cl = 85.7(2), C(1)–In–C(6) = 133(2), In–P–In′ = 92.8(2), Si–P–Si′ = 106.8(3), In–Cl–In′ = 95.8(3).

Crystals of **2** suitable for X-ray analysis were obtained by recrystallization from pentane. Compound **2** is isostructural with **9**, but their crystals are not isomorphous. Whereas compound **9** crystallizes in the triclinic system with two molecules in the unit cell occupying the general positions of the centrosymmetric space group $P\bar{1}$, crystals of **2** belong to the monoclinic system, space group $C2/c$, with four molecules in the unit cell lying on crystallographic C_2 symmetry axes. An ORTEP diagram of **2** showing the atom-numbering scheme is presented in Figure 2. In **9**, the Cl atom is displaced by 1.020 Å from the In–P–In plane and thus the In–P–In–Cl ring is distinctly puckered. In crystals of **2**, the molecules lie on a crystallographic C_2 symmetry axis which passes through the P and Cl atoms, thereby suggesting that the In–P–In–Cl ring is exactly planar. The extremely large anisotropic displacement parameter of the Cl atom perpendicular to the ring plane [U_{33} = 0.70(2) Å^2 ≫ U_{11} = 0.140(6) Å^2 > U_{22} = 0.089(6) Å^2] and those of the neopentyl carbon atoms indicate that the crystals in reality contain molecules of **2** in which the ring is also puckered but wherein the sites are occupied by pairs of molecules folded in the opposite sense. The apparent considerable foreshortening of the In–Cl bond length to 2.560(7) Å in **2** from the mean of 2.621 Å in **9** is a result of this partial site occupancy. The In–P distance of 2.622(5) Å in **2** is slightly greater than the mean of 2.603 Å in **9**. In–P–In and P–In–Cl bond angles of 92.8(2) and 85.7(2)°, respectively, in **2** lie close to corresponding values of 90.6(1)° and a mean of 85.1° in **9**; the difference between the In–Cl–In′ angles, 95.8(3)° in **9** ≫ 89.8(1)° in **2**, is a direct consequence of the averaged planar ring geometry in the latter.

As was previously noted, the room temperature reaction of $(Me_3CCH_2)_2InCl$ and $P(SiMe_3)_3$ in a 1:1 mole ratio affords **2** as the major product in addition to a viscous yellow oil that is mainly composed of unreacted $P(SiMe_3)_3$. However, after one such experiment, a small amount (*ca.* ~2%) of another material was detected in the ^1H NMR spectrum of the resulting oil. Allowing the oil to stand refrigerated for several days resulted in the growth of a few crystals along the sides of the vessel. X-ray crystallographic analysis identified these crystals as being the compound $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)$ (**3**).

The isolation of **3**, though a minor product, is noteworthy, as it constitutes the first example of an In–P–In–P-containing species in which the two phosphorus centers are not symmetrically substituted. Compound **3** is a yellow crystalline solid that is very unstable at room temperature under an inert atmosphere and rapidly decomposes upon standing in hydrocarbon solution. Its ^1H, $^{13}C\{H\}$, and $^{31}P\{H\}$ NMR spectra are consistent with the solid-state structure (*vide infra*). Thus, coupling of the two different $SiMe_3$ groups with the phosphorus nuclei gives rise to two doublet resonances in the ^1H and $^{13}C\{H\}$ NMR spectra. Morover, the $^{31}P\{H\}$ NMR spectrum contains two sharp resonances identifiable with the two unique phosphorus atoms while the ^{31}P nondecoupled NMR shows splitting of one of these signals by the attached proton.

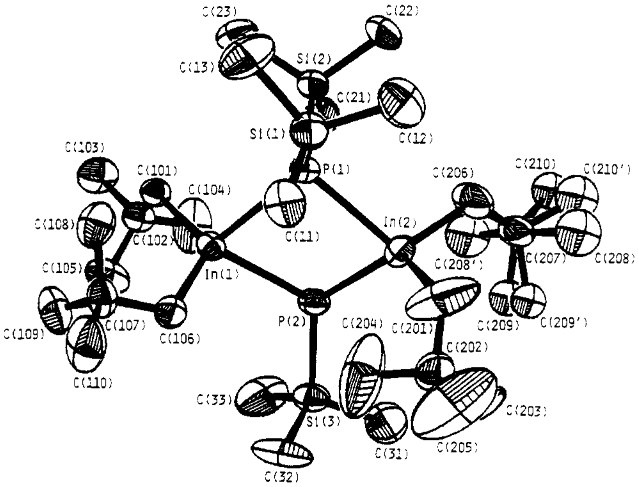

Figure 3. ORTEP diagram (30% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of $(Me_3CCH_2)_2InP(SiMe_3)_2In(CH_2CMe_3)_2PH(SiMe_3)$ (**3**). The methyl carbon atoms of one of the neopentyl groups are disordered over two orientations. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): In(1)–P(1) = 2.669(2), In(1)–P(2) = 2.650(3), In(2)–P(1) = 2.644(3), In(2)–P(2) = 2.638(2), In–C = 2.17(1)–2.25(2), P(1)–Si(1) = 2.252(4), P(1)–Si(2) = 2.248(3), P(2)–Si(3) = 2.248(4); P(1)–In(1)–P(2) = 82.43(7), C(101)–In(1)–C(106) = 124.8(4), P(1)–In(2)–P(2) = 83.12(7), C(201)–In(2)–C(206) = 112.8(8), In(1)–P(1)–In(2) = 94.52(7), In(1)–P(2)–In(2) = 95.08(7), In(1)–P(2)–Si(3) = 123.0(1), In(2)–P(2)–Si(3) = 127.9(1).

Compound **3** crystallizes in the triclinic system with two molecules in the unit cell occupying the general positions of the centrosymmetric space group $P\bar{1}$. Figure 3 presents an ORTEP diagram of **3** showing the atom-numbering scheme. The dihedral angle between the In(1)–P(1)–In(2) and In(1)–P(2)–In(2) planes is 24.7° [mean magnitude of the endocyclic torsion angle about the ring bonds = 16.6°], and thus the In–P–In–P core in **3** is distinctly puckered. This ring geometry contrasts with the planar In–P–In–P rings encountered in other compounds in which there is at least one hydrogen atom bonded to each of the phosphorus atoms, *viz.* $[(Me_3SiCH_2)_2InP(H)R]_2$ [R = adamantyl (**10**);[23] R = Me_3C (**11**)[24]]. The mean In–P bond length of 2.650 Å in **3** lies within the range of 2.659 Å in **10** and 2.635 Å in **11**, and it is similar to the mean of 2.655 Å in **8**[14] but longer than that of 2.637 Å in **1**. In **3**, the mean of the essentially equal P–Si bonded distances at 2.249 Å is similar to that of 2.254 Å in **1**. The mean In–P–In bond angle at 94.8° in **3** is slightly smaller than the virtually equal angles of 98.2° in **10** and 98.3° in **11**, probably due to the increased steric compression about the phosphorus atoms in **3** (i.e., **10** and **11** each have two sterically less demanding hydrogen atoms at each of the phosphorus centers in contrast to only one such center in **3**). The P–In–P bond angle of 82.77° in the puckered ring of **3** is slightly enlarged over those of 81.8(1) and 81.7(1)° in the planar rings of **10** and **11**, respectively. The significantly different values of the exocyclic bond angles subtended at the In centers in **3** [112.8(8) and 124.8(4)°] despite their identical chemical environment reflect the ease of deformation of such bond angles in response to variations in intra- and intermolecular steric factors.

Acknowledgment. We wish to thank the Office of Naval Research, the Air Force Office of Scientific Research, and the Lord Foundation of North Carolina for their financial support.

Supplementary Material Available: Tables of crystallographic data and measurements, hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and complete interatomic distances and angles, including torsion angles, for **1**–**3** (17 pages). Ordering information is given on any current masthead page.

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