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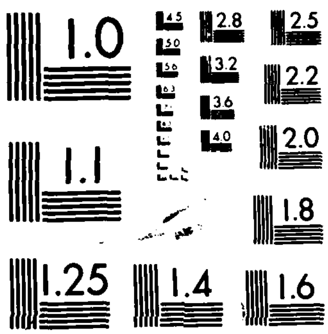

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The new amphoteric ligands $(Me_3SiCH_2)_2GaPPh_2$, $(Me_3SiCH_2)_2InPPh_2$, and $(Me_3CCH_2)_2InPPh_2$ have been prepared and characterized by elemental analyses, cryoscopic molecular weight measurements and ^1H NMR, ^{31}P NMR and IR spectroscopic data. An X-ray structural study was also used to define the nature of $[(Me_3SiCH_2)_2InPPh_2]_2$ in the solid state. These compounds have been prepared by either of two methods, a thermolysis reaction between the group 13 metal trialkyl and PPh_2H or by a metathetical reaction between the dialkylmetal halide and $KPPh_2$. Cryoscopic molecular weight measurements and

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20. Abstract (continued)

^{31}P NMR spectroscopic data demonstrate that the new compounds exist as monomer-dimer equilibrium mixtures in benzene solution. The colorless crystal of $[(Me_3SiCH_2)_2InPPh_2]_2$ contains two discrete molecules of the dimer in each unit cell. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions of a = 10.323(4)Å, b = 11.113(5)Å, c = 21.509(8)Å, α = 83.85(5)°, β = 86.66(6)°, γ = 83.27(5)° and ρ_{calcd} = 1.29, β = 86.66(6)°, γ = 83.27(5)° and ρ_{calcd} = 1.29 g/cm^3. Full matrix least-squares refinement led to a final R value of 0.035 for 3787 observed reflections. The molecule contains four membered indium-phosphorus rings.

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TECHNICAL REPORT NO. 17

Synthesis and Characterization of Amphoteric Ligands Including the Crystal and Molecular Structure of $[(Me_3SiCH_2)_2InPPh_2]_2$

by

O. T. Beachley, Jr., John P. Kopasz, Hongming Zhang,

William E. Hunter and Jerry L. Atwood

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University of Alabama, University, Alabama 35486)

Synthesis and Characterization of Amphoteric Ligands Including the Crystal and Molecular Structure of $[(Me_3SiCH_2)_2InPPh_2]_2$ *

by

O. T. Beachley, Jr.,[1a] John P. Kopasz,[1a] Hongming Zhang,[1b] William E. Hunter[1b] and Jerry L. Atwood[1b]

Abstract

The new amphoteric ligands $(Me_3SiCH_2)_2GaPPh_2$, $(Me_3SiCH_2)_2InPPh_2$, and $(Me_3CCH_2)_2InPPh_2$ have been prepared and characterized by elemental analyses, cryoscopic molecular weight measurements and ^1H NMR, ^{31}P NMR and IR spectroscopic data. An X-ray structural study was also used to define the nature of $[(Me_3SiCH_2)_2InPPh_2]_2$ in the solid state. These compounds have been prepared by either of two methods, a thermolysis reaction between the group 13 metal trialkyl and PPh_2H or by a metathetical reaction between the dialkylmetal halide and $KPPh_2$. Cryoscopic molecular weight measurements and ^{31}P NMR spectroscopic data demonstrate that the new compounds exist as monomer-dimer equilibrium mixtures in benzene solution. The colorless crystal of $[(Me_3SiCH_2)_2InPPh_2]_2$ contains two discrete molecules of the dimer in each unit cell. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions of a = 10.323(4)A, b = 11.113(5)A, c = 21.509(8)A, α = 83.85(5)°, β = 86.66(6)°, γ = 83.27(5)° and ρ_{calcd} = 1.29

$\beta = 86.66(6)°$, $\gamma = 83.27(5)°$ and $\rho_{calcd} = 1.29\ g/cm^3$. Full matrix least-squares refinement led to a final R value of 0.035 for 3787 observed reflections. The molecule contains four membered indium-phosphorus rings.

* Dedicated to Professor G. E. Coates on the occasion of his 70th birthday.

Introduction

Compounds of the general type $R_2MBR'_2$ in which M is a Lewis acid from group 13 and B is a group 15 Lewis base are of current interest. These compounds can remain as monomers with the potential for π-bonding[2], can associate to form dimers, trimers or higher oligomers[2] and/or can react as amphoteric ligands in transition metal organometallic chemistry.[3] In addition, some examples from this class of compounds have been used to make semiconductor materials by the MOCVD process.[4]

A goal of our research is the elucidation of the effects of bulky ligands on the properties of main-group compounds. Since amphoteric molecules have two distinct parts, the acidic and the basic ends of the molecule, it is possible to introduce bulky substituents into one portion of the molecule and to investigate their effects on the chemistry of the amphoteric species. For example the presence of bulky substituents on the main-group metal might significantly alter its Lewis acidity but have minimal effects on the basicity of the group 15 atom. The compounds Me_2AlPPh_2[5,7] and Et_2AlPPh_2[6,7] exist as dimers in benzene solution and do not react with $Cr(CO)_5NMe_3$[3]. The related molecule with bulky trimethylsilylmethyl substituents on aluminum exists as a monomer-dimer equilibrium mixture in benzene solution according to cryoscopic molecular weight measurements[7] and reacts readily with $Cr(CO)_5NMe_3$ to form $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2{\cdot}NMe_3]$[3]. This reactivity pattern for this limited range of amphoteric organoaluminum-phosphorus ligands with $Cr(CO)_5NMe_3$ has been proposed to be related to the presence or absence of the monomeric ligand species.[3] In order to test this hypothesis further, the chemistry of related amphoteric molecules with other group 13 atoms should be investigated. The Lewis acidity of the amphoteric molecule should decrease in the order[2] Al > Ga > In but the Lewis basicity of the $-PPh_2$ portion of the molecule might not be expected to change significantly.

In this paper we report the synthesis and characterization of $(Me_3SiCH_2)_2GaPPh_2$, $(Me_3SiCH_2)_2InPPh_2$ and $(Me_3CCH_2)_2InPPh_2$. These compounds permit us to investigate the effects of the group 13 metal as well as to compare the effects of two closely related bulky substituents, trimethylsilylmethyl and neopentyl, on the properties of the amphoteric compounds. The compounds have been characterized by elemental analyses, cryoscopic molecular weight studies and IR, ^1H and ^{31}P NMR spectroscopic data. The compound $[(Me_3SiCH_2)_2InPPh_2]_2$ has also been characterized by an X-ray structural study.

Experimental Section

General Data All compounds described in this investigation were oxygen and moisture sensitive and were manipulated in a purified argon atmosphere or under vacuum. The solvents were purified by conventional means and were vacuum distilled prior to use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of Perkin-Elmer Model 683 spectrometer. Absorption intensities are reported with abbreviations w(weak), m(medium), s(strong) and sh(shoulder). The ^1H NMR spectra were recorded at 90 and 270 MHz by using Varian Model EM-390 and Jeol Model FX 270 spectrometers, respectively. Chemical shifts are reported in δ units (ppm). ^1H NMR spectra are referenced to benzene at δ 7.13. The $^{31}P\{^1H\}$ NMR spectra were recorded at 109.16 MHz by using a Jeol Model FX 270 spectrometer and are referenced to 85% H_3PO_4 at δ 0.00ppm. The molecular weights were measured cryoscopically in benzene solution using an instrument similar to that described by Shriver.[8] Diphenylphosphine was purchased from

Strem Chemicals, Inc. and was vacuum distilled prior to use. The reagents $Ga(CH_2SiMe_3)_3$,[9] $Ga(CH_2SiMe_3)_2Br$[9], $In(CH_2SiMe_3)_3$[10] and $KP(C_6H_5)_2$[7] were prepared by literature procedures. The compounds $In(CH_2SiMe_3)_2Br$ and $In(CH_2SiMe_3)_2I$ were prepared by stoichiometric ligand redistribution reactions in benzene using the appropriate indium trihalide.

$In(CH_2SiMe_3)_2Br$: mp 93.5-94.5°C. ^1H NMR (benzene) 0.36 s (2H, CH_2), 0.15s (9H, Me). $In(CH_2SiMe_3)_2I$: mp 64-65.5°C. ^1H NMR (benzene) 0.64 s (2H, CH_2), 0.18 s (9H, Me).

Synthesis of $(Me_3SiCH_2)_2InPPh_2$. $(Me_3SiCH_2)_2InPPh_2$ was synthesized by four methods.[1] The preferred preparative route was the thermolysis of $In(CH_2SiMe_3)_3$ and PPh_2H in pentane. When this method was employed the indium phosphide precipitated from the reaction solution at 55°C as a colorless crystalline product which simplified purification of the product.

(a) From $In(CH_2SiMe_3)_3$ and PPh_2H in Pentane. The reagents, 3.015 g (8.010 mmol) of $In(CH_2SiMe_3)_3$ and 1.492 g (8.013 mmol of PPh_2H, were combined in a reaction tube equipped with a Teflon valve and stir bar using the dry box. The reaction vessel was evacuated and finally heated at 55°C for 3 days. Crystals of $(Me_3SiCH_2)_2InPPh_2$ formed during heating. After cooling the reaction mixture to -78°C, the crystalline solid product was isolated by filtration. Two final washings with 10 mL of pentane at -20°C provided colorless crystals of $(Me_3SiCH_2)_2InPPh_2$ (3.57 g, 7.53 mmol, 94.0% yield based on $In(CH_2SiMe_3)_3$). $(Me_3SiCH_2)_2InPPh_2$: mp 152°C dec.. Anal. Calcd: 50.63% C, 6.80% H. Found: 50.27% C, 6.67% H. ^1H NMR (benzene, 0.42 m) δ 0.13 t (J = 1.8Hz 2H, CH_2), 0.04s (9H, Me). ^{13}C NMR (benzene) δ 2.98q (J = 119Hz, CH_3), -0.18 triplet of triplets (J_1 = 117Hz, J_2 = 8Hz, CH_2). (See Results and Discussion.) $^{31}P\{^1H\}$ NMR (benzene, 0.01m), (δ, (relative peak height)) species: -29.1 s, (-), monomer; (benzene, 0.44 m) -29.15 s (12.23) monomer, -50.30 s, (1), dimer. IR (Nujol mull, cm^{-1}) 2320 (w), 1970 (vw), 1945 (vw), 1930 (vw), 1885 (vw,br), 1870 (vw), 1807 (vw), 1660 (w), 1642 (w), 1581 (m), 1480 (s), 1432 (s), 1353 (m), 1349 (m), 1322 (vw), 1300 (w), 1252 (m), 1240 (vs), 1180 (w), 1155 (w), 1092 (w), 1065 (w), 1024 (m), 967 (s), 960 (s,sh), 955 (s), 940 (s), 927 (m), 910 (w), 905 (vw,sh), 845 (vs), 837 (vs), 821 (vs), 740 (s,sh), 734 (vs), 712 (s), 689 (s), 681 (m,sh), 607 (vw), 570 (m), 552 (m), 500 (m), 489 (m), 471 (m), 440 (w), 345 (vw), 270 (w). Cryoscopic molecular weight, formula weight $(Me_3SiCH_2)_2InPPh_2$ 474.4 (calcd. molality, obs. molality, assoc.): 0.1267, 0.0801, 1.58; 0.0781, 0.0575, 1.36; 0.0565, 0.0436, 1.29; 0.1414, 0.0933, 1.52; 0.0873, 0.0630, 1.39; 0.0631, 0.0470, 1.34. Crystallographic quality crystals were obtained from a saturated pentane: benzene mixture (2:1) at 0°C. (b). From $In(CH_2SiMe_3)_3$ and PPh_2H in Benzene. The compound $(Me_3SiCH_2)_2InPPh_2$ was prepared as described above except the pentane was replaced by benzene. After heating the reaction mixture at 55°C for 7 days, the vessel was opened to the vacuum line and the $SiMe_4$ produced was collected by fractionation through two -78C° traps and isolation in a -196°C trap. The $SiMe_4$ (7.58 mmol, PVT measurements, 95% yield based on $In(CH_2SiMe_3)_3$) was identified by its ^1H NMR spectrum. The indium-phosphide was then washed out of the reaction tube with benzene and the benzene was finally removed by vacuum distillation. The remaining solid was recrystallized from 20 mL of pentane at -78C° to yield 3.534 g (7.449 mmol, 93.0% yield) of $(Me_3SiCH_2)_2InPPh_2$. Spectral properties of the indium-phosphide from this preparation were identical to the product obtained from reaction in pentane. (c). From $KPPh_2$ and $In(CH_2SiMe_3)_2Br$ in Et_2O. A solution of 0.823 g (2.23 mmol) of $In(CH_2SiMe_3)_2Br$ dissolved in 40 mL of Et_2O was combined with 0.500 g of $KPPh_2$(2.23 mmol) with stirring over a 15 minute period. Upon addition of the $KPPh_2$, a white precipitate formed immediately. The mixture was stirred for 24 hours and then the ether was removed by vacuum distillation. The product mixture was extracted 5 times with 25 mL of pentane each to separate the product from KBr. The indium phosphide was finally washed once with pentane at -20°C. After the pentane was removed, 0.670 g (1.40 mmol, 62.7% yield based on $In(CH_2SiMe_3)_2Br$) of $(Me_3SiCH_2)_2InPPh_2$ was isolated. Spectral properties of the indium phosphide obtained from this preparative route were identical to those obtained for the product from the thermolysis reaction in pentane. Similar results were obtained when $In(CH_2SiMe_3)_2I$ and $KPPh_2$ were used.

Synthesis of $(Me_3SiCH_2)_2GaPPh_2$. Potassium diphenylphosphide (0.465 g, 2.07 mmol) was slowly added to a room temperature solution of 0.675 g (2.07 mmol) of $Ga(CH_2SiMe_3)_2Br$ over a 10 minute period. A white precipitate formed upon the addition of $KPPh_2$. The mixture was then stirred for 10 hours. After this time, the Et_2O was removed by vacuum distillation and replaced by 40 mL of pentane. The gallium-phosphide was separated from KBr with 5 washings of 40 mL of pentane each. Finally, after the pentane was removed 0.205 g (1.72 mmol, 83.1% yield based on $KPPh_2$) of KBr and 0.730 g (1.70 mmol, 82.1% based on $KPPh_2$) of $(Me_3SiCH_2)_2GaPPh_2$ had been separated. The gallium-phosphide was finally recrystallized from pentane at -78°C. $(Me_3SiCH_2)_2GaPPh_2$. Colorless, crystalline solid; mp 121 - 146°C a glass forms that melts at 154 - 156°C. Anal. Calcd: C, 55.94%, H, 7.51%. Found: C, 55.64%, H, 7.70%. Hydrolysis: 1.97 mol $SiMe_4$/mol $(Me_3SiCH_2)_2GaPPh_2$. IR (Nujol mull, cm^{-1}): 2420 (w), 1965 (vw), 1945 (vw), 1880 (vw), 1810 (vw), 1580 (m), 1575 (w,sh), 1350 (m), 1301 (m), 1251 (m,sh), 1240 (vs), 1170 (w), 1167 (w), 1154 (w), 1090 (w), 1065 (w), 1023 (m), 995 (s,sh), 985 (s), 963 (m), 947 (m), 912 (w), 848 (vs), 839 (s,sh), 820 (vs), 747 (s,sh), 737 (s,sh), 732 (vs), 718 (s), 690 (s), 680 (s,sh), 665 (m,sh), 613 (w), 583 (m), 558 (m), 524 (m), 500 (m), 476 (m), 458 (w), 440 (vw), 420 (vw), 390 (vw), 370 (vw), 320 (vw), 232 (vw). Cryoscopic molecular weight, formula weight $(Me_3SiCH_2)_2GaPPh_2$ 429.3 (calcd. molality, obs. molality, assoc.): 0.1545, 0.0808, 1.91; 0.0966, 0.0597, 1.61; 0.0702, 0.0456, 1.54. ^1H NMR (benzene, 0.54 m) δ 0.21 t (J = 3.5Hz, 2H, CH_2), 0.01 s (9H, Me). $^{31}P\{^1H\}$ NMR δ, (relative peak height), species: (benzene, 0.1 m) -27.2 s (7.7), monomer; -40.4 s (1), dimer; (benzene, 0.01 m) -27.2 s (27.7), monomer; -40.25 s (1), dimer.

Reaction of $Ga(CH_2SiMe_3)_3$ and PPh_2H. The reagents, 1.063 g (3.208 mmol) of $Ga(CH_2SiMe_3)_3$ and 0.597 g (3.21 mmol) of PPh_2H, were combined in 8 mL benzene in a reaction tube equipped with a break-seal side arm. After the reaction tube was sealed, it was placed in an oven and heated to 160 - 165° for 3 weeks. The break seal was then opened, and the volatile components were removed and fractionated through two -78° traps and a -196° trap. The tetramethylisilane which formed during the reaction (1.77 mmol, PVT measurements 55.1% based on PPh_2H) was collected in the -196°C trap. Since the measurements of the evolved $SiMe_4$ indicated that the reaction was incomplete, the product was not isolated but a ^{31}P NMR spectrum of a benzene solution of the resulting nonvolatile solid was recorded. $^{31}P\{^1H\}$ NMR benzene, δ, (relative peak height): -14.6 (1.0), -27.4 (1.8), -35.5 (3.1).

Reaction of $(Me_3SiCH_2)_2GaPPh_2$ and PPh_2H. The reagents, 0.100 g (0.233 mmol) of $(Me_3SiCH_2)_2GaPPh_2$ and 0.050 g (0.27 mmol) of PPh_2H were combined in an NMR tube using the dry box. After benzene was distilled into the tube, the tube was sealed under vacuum. $^{31}P\{^1H\}$ NMR (benzene), δ, (relative peak height) -27.01, (1.0), -40.16, (2.1).

Reaction of $(Me_3SiCH_2)_2GaPPh_2$ with $Ga(CH_2SiMe_3)_3$. A mixture of $(Me_3SiCH_2)_2GaPPh_2$ (0.100 g, 0.233 mmol) and $Ga(CH_2SiMe_3)_3$ (0.105 g, 0.317 mmol) in 3 mL of benzene in a sealed NMR tube was observed by ^{31}P NMR spectroscopy. $^{31}P\{^1H\}$ NMR, (benzene), δ, (relative peak height) -14.1 (1), -26.7 (8).

Synthesis of $(Me_3CCH_2)_2InPPh_2$. The new compound $(Me_3CCH_2)_2InPPh_2$ was prepared from $In(CH_2CMe_3)_3$ (0.873 g, 2.66 mmol) and PPh_2H (0.495 g, 2.66 mmol) in benzene using the method previously described for $(Me_3SiCH_2)_2InPPh_2$. The reaction mixture was heated at 60°C for 3 days. The neopentane which formed during the reaction was separated from benzene by passing the neopentane through two -78°C traps and was collected in a -196°C trap. Neopentane CMe_4 (2.57 mmol, PVT measurements, 96.6% yield based on $In(CH_2CMe_3)_3$) was isolated. The colorless solid remaining after the removal of the neopentane and benzene was washed once with 20 mL pentane at -78°C to leave $(Me_3CCH_2)_2InPPh_2$ (0.815 g, 1.84 mmol, 69.3% yield based on $In(CH_2CMe_3)_3$). $(Me_3CCH_2)_2InPPh_2$. mp 138 - 143°C a glass forms that decomposes at 143 - 150°C. Anal. Calcd: C, 59.74%, H, 7.29%. Found:. C, 59.74%, H, 7.13. ^1H NMR (benzene, 0.40 m) 1.47 t (J = 2.4Hz, 1H, CH_2), 1.10 s (3.5H, CH_3), 1.03 s (1H, CH_3); (benzene, 0.20 m) 1.47 t (J = 2.4Hz, 1.2H, CH_2), 1.07 s (4.9H, CH_3), 1.03 s (1.0H, CH_3). (See Results and Discussion.) $^{31}P\{^1H\}$ NMR: (benzene, 0.28 m), δ, (relative peak height), species: -29.95 s (5.2) monomer, -49.40 (1.0) dimer; (benzene, 0.02 m) -29.95 s (5.4) monomer, -49.40 (1.0) dimer. IR (Nujol mull, cm^{-1}): 1960 (w), 1943 (w), 1875 (w,br), 1802 (w), 1740 (w), 1580 (m), 1567 (w), 1354 (s), 1297 (m), 1270 (w,br) 1230 (s), 1205 (w,sh), 1170 (w), 1160 (w,sh), 1150 (w), 1125 (vw), 1110 (w), 1096 (w), 1090 (w), 1061 (w), 1040 (vw), 1020 (w), 1009 (w), 998 (w), 965 (w,br), 907 (w), 890 (w), 840 (w), 765 (w,br), 736 (sh), 729 (vs), 717 (m), 687 (vs), 616 (s), 609 (m), 568 (m), 556 (m,sh), 540 (w), 497 (m), 468 (m), 445 (w), 430 (w), 375 (vw), 345 (w), 255 (w). IR (Kel-F mull): 3080 (w), 3060 (w), 2960 (vs), 2940 (s,sh), 2890 (m), 2870 (m), 2320 (w,br), 2200 (w), 1950 (vw), 1880 (vw,br), 1810 (w), 1785 (w), 1735 (w), 1585 (w), 1575 (w), 1478 (s,sh), 1470 (s), 1437 (s), 1440 (m,sh), 1385 (m), 1365 (s), 1360 (s). Cryoscopic molecular weight, formula weight $(Me_3CCH_2)_2InPPh_2$ 442.25 (calcd. molality, obs. molality, assoc.): 0.175, 0.087, 2.01; 0.107, 0.057, 1.88; 0.077, 0.043, 1.80.

Crystallographic Studies. A single crystal of $[(Me_3SiCH_2)_2InPPh_2]_2$ was sealed under an N_2 atmosphere in a thin-walled glass capillary. The crystal was mounted and data were collected on a Enraf-Nonius CAD-4 diffractometer by the $\omega/2\theta$ scan technique. The reflection data were corrected for Lorentz and polarization effects but not for absorption effects. A summary of the data collection parameters and final lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 25 high angle reflections ($2\theta > 35°$) accurately centered on the diffractometer are given in Table 1.

Solution and Refinement of the Structure. The space group for the crystal, P1, was verified by the successful refinement. At first the centrosymmetric space group $P\bar{1}$ was selected to solve the structure but all attempts failed. The distribution of $|E|$ values did not provide clear information whether or not the structure was centric. Then, the space group was changed to P1 and direct methods (MULTAN 80)[11] provided the four indium atoms. However, large correlations of related parameters appeared in the least-squares refinement. Therefore, the structure was transformed to the higher symmetry of $P\bar{1}$ by moving the origin of the unit cell. The coordinates of the other nonhydrogen atoms were obtained from the subsequent calculations of difference syntheses. Neutral atom scattering factors for

C, In, P and Si were taken from Cromer and Waber.[12] The full-matrix least squares refinement with isotropic temperature factors with the SHELX 76[13] program system led to the reliability index of $R = \Sigma (|F_o|-|F_c|)/\Sigma|F_o| =$ 0.066, then with anisotropic thermal parameters for all nonhydrogen atoms gave the final values of R = 0.035 and $R_w = \{\Sigma w (|F_o|-|F_c|)/\Sigma w |F_o|^2\}^{1/2} =$ 0.042 based on 3787 observed reflections ($I > 2\sigma(I)$). The function minimized in the least squares calculations was $\Sigma w|\Delta F|^2$ with unit weights. In the last cycle of refinement no parameters shifted by more than 0.005 of its estimated standard deviation. A final difference Fourier showed no feature greater than 0.34e/A^3. No effort to find hydrogen atoms was made. The final parameters of the positional and thermal parameters are given in Table II.

Results and Discussion

A series of new amphoteric molecules, $(Me_3SiCH_2)_2InPPh_2$, $(Me_3CCH_2)_2InPPh_2$ and $(Me_3SiCH_2)_2GaPPh_2$ have been prepared and characterized. The characterization data include elemental analyses, cryoscopic molecular weight measurements as well as IR, ^1H and ^{31}P NMR spectroscopic data. A variety of data for benzene solutions of the new compounds suggest that they exist as equilibrium mixtures of monomers and dimers. In contrast, the X-ray structural study reveals the presence of the dimer, $[(Me_3SiCH_2)_2InPPh_2]_2$, in the solid state.

The organometallic phosphides have been prepared by two methods: (1) the thermolysis of a mixture of MR_3 and PPh_2H (equation 1) and (2) the metathetical reaction between R_2MBr and $KPPh_2$ (equation 2). However, the preferred method for the preparation of the indium phosphides was the thermolysis route but the metathetical reaction was more useful for preparing $(Me_3SiCH_2)_2GaPPh_2$. The extent of the thermolysis reaction was determined by

$$MR_3 + PPh_2H \xrightarrow[C_6H_6]{C_5H_{12}} \text{ or } \quad R_2MPPh_2 + RH \qquad (1)$$

$$MR_2Br + KPPh_2 \xrightarrow{Et_2O} R_2MPPh_2 + KBr_{(s)} \qquad (2)$$

the isolation of pure RH ($SiMe_4$, R = CH_2SiMe_3 and CMe_4, R = CH_2CMe_3). For the reactions of organoindium compounds the yields of RH were typically greater than 95%. However, when $Ga(CH_2SiMe_3)_3$ was used, $SiMe_4$ was produced in less that 60% yield, even after heating at 160 - 165°C for 3 weeks. In the case of metathetical reactions, KBr was usually isolated in greater than 80% yields. When a given compound was prepared by both methods, identical chemical and spectroscopic properties were observed for the products. However, it is of significance to note that the melting points of these amphoteric metal-phosphides are not useful for estimating the purity of a sample. The organoindium compounds decompose before melting and the gallium-phosphide undergoes a transition to a glass prior to melting. The presence of the glass makes the observation of the melting point difficult and possibly unreliable. Similar phase changes have been observed for $(Me_3SiCH_2)_2AlPPh_2$[7] as well as for other examples of this class of compound.[5,14,15] These glass transitions have been suggested to be due to changes in the degree of association.[14,15]

The thermolysis of $Ga(CH_2SiMe_3)_3$ and PPh_2H produced $SiMe_4$ in less than 60% yield. Prolonged heating of a reaction mixture at 160 - 165°C did not even succeed in driving the reaction to completion. Other attempts to force the elimination by raising the temperature above 165°C led to the decomposition of the gallium-phosphide product. The cause of the incomplete elimination of $SiMe_4$ from $Ga(CH_2SiMe_3)_3$ and PPh_2H was investigated by using ^{31}P NMR spectroscopy. The data suggest that the formation of an adduct between $(Me_3SiCH_2)_2GaPPh_2$ and $Ga(CH_2SiMe_3)_3$ reduces the concentration of free $Ga(CH_2SiMe_3)_3$ available for an elimination reaction with PPh_2H, thereby slowing the rate of the elimination reaction. (These data are discussed fully later in the discussion.) As the amount of $(Me_3SiCH_2)_2GaPPh_2$ increases, the concentration of the adduct increases and the rate of reaction decreases further. The formation of an adduct between an organometallic phosphide and a group III alkyl has also been invoked to explain kinetic data and the long times required for complete conversion of $AlMe_2H$-P(Me)(Ph)H mixture to H_2 and $Me_2AlP(Me)(Ph)$.[16]

The crystal of $[(Me_3SiCH_2)_2InPPh_2]_2$ consists of discrete isolated molecules. There are two molecules in the asymmetric unit and each lies on a crystallographic center of inversion. Molecule A with the atom numbering scheme is shown in Figure 1; the structure of molecule B is very similar to that of molecule A. However, the dimensions of the four-membered indium-phosphorus rings of the two kinds of molecules are slightly different. In molecule A the nonbonding distance of In•••In' and P•••P', within the rings are 3.9670(7) and 3.524(3)A while in molecule B are 3.9992(7) and 3.464(3)A, respectively. Bond distances and angles are listed in Table 3. From this comparison, slight differences are apparent: the angles P-In-P' = 83.23(7)° and In-P-In^1 = 96.77(7)° in molecule A while 81.80(7)° and 98.20(8)°, respectively, are found in molecule B. The In-P distances vary from 2.632(2) to 2.664(2)A and all these values are shorter than the mean value of 2.712A for bis(triphenylphosphine)-trichloroindium(III).[17] The In-C bond lengths vary from 2.196(8) to 2.209(8)A, (average 2.202[8]A). These are close to those found in other organoindium compounds, such as $InMe_3$ (2.12, 2.06, 2.15Å)[18], $Et_2InOOCMe_3$(2.22, 2.29Å)[19], $Me_2InOOCMe_3$ (2.11, 2.08Å)[20], $(Me_2InNMe_2)_2$ (2.168, 2.170Å)[21] and $[Me_2InN(Me)(Ph)]_2$ (2.149, 2.156Å)[22]. The C-In-C angles are wide at 127.8(3)° and 125.9(3)° because of steric hindrance between the bulky CH_2SiMe_3 groups. Figure 2 shows the packing of molecules in the unit cell of the compound. No short contacts are noted.

The apparent degree of association of each compound R_2MPPh_2 (M = Ga, R = CH_2SiMe_3; M = In, R = CH_2SiMe_3, CH_2CMe_3) in benzene solution was studied by means of cryoscopic molecular weight measurements. These studies indicate that monomer-dimer equilibria occur in benzene solution. The average degree of association of the trimethylsilylmethyl derivatives at a given concentration decreases in the order Al[6] > Ga > In. This order follows the order expected on the basis of Lewis acidity.[1] It is also of interest that the neopentyl indium derivative is more associated than the corresponding trimethylsilylmethyl derivative. The observations of the higher degree of association of the neopentyl compounds in comparison to the CH_2SiMe_3 derivatives might suggest that the electronic effects of the neopentyl group enhance the Lewis acidity of the group 13 atom. Alternatively, the neopentyl group would have to be sterically less demanding than the trimethylsilymethyl group, a hypothesis which is inconsistent with the general literature. Calculations using group electronegativities[23] indicate that a higher positive charge is located on the metallic center of the neopentyl-indium phosphide than on the indium of the trimethylsilylmethyl derivative. Consequently, the neopentyl derivatives are expected to have a greater Lewis acidity than the trimethylsilylmethyl analog.

The intensities of the lines in ^{31}P NMR spectra of the organometallic phosphides R_2MPPh_2 (M = Ga, R = CH_2SiMe_3; M = In, R = CH_2SiMe_3, CH_2CMe_3) are concentration dependent over the concentration range from 0.01 to 0.50m and are consistent with the occurrence of monomer-dimer equilibria. A typical spectrum consists of two resonances: one at approximately -30ppm, and the second between -40 and -50ppm. The relative peak heights of the upfield resonance to the downfield resonance increased as the concentration of the organometallic phosphide increased but the chemical shifts of the lines did not change. These observations suggest that the upfield signal is due to the phosphorus atoms of the dimeric species and the downfield resonance is due to the monomeric species. In the case of $(Me_3SiCH_2)_2InPPh_2$, only the monomeric species was observed at low concentrations, whereas resonances for both the monomeric and dimeric species were observed at all concentrations studied for $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3CCH_2)_2InPPh_2$. These observations are consistent with group electronegativity calculations[23] of partial charges on gallium and indium. The indium atom in $(Me_3SiCH_2)_2InPPh_2$ has the lowest calculated partial positive charge and the lowest degree of association.

The presence of an adduct of the gallium-phosphide with $Ga(CH_2SiMe_3)_3$, $(Me_3SiCH_2)_2GaPPh_2 \cdot Ga(CH_2SiMe_3)_3$, among the thermolysis products from $Ga(CH_2SiMe_3)_3$ and PPh_2H was suggested by comparing the $^{31}P\{^1H\}$ NMR spectrum of the thermolysis mixture with that for pure $(Me_3SiCH_2)GaPPh_2$ and for mixtures of pure $(Me_3SiCH_2)_2GaPPh_2$ with added $Ga(CH_2SiMe_3)_3$ or with added PPh_2H. The ^{31}P NMR spectrum of the product mixture after thermolysis (no purification) exhibited resonances at -14.6, -27.4 and -35.5ppm, which are assigned to $(Me_3SiCH_2)_2GaPPh_2 \cdot Ga(CH_2SiMe_3)_3$, monomeric $(Me_3SiCH_2)_2GaPPh_2$ and an unknown species, respectively. The line at -14.6 ppm which is attributed to $(Me_3SiCH_2)_2GaPPh_2 \cdot Ga(CH_2SiMe_3)_3$ has a very similar shift to the line at -14.6 ppm in the spectrum of a mixture $(Me_3SiCH_2)_2GaPPh_2$ and $Ga(CH_2SiMe_3)_3$. The resonance for the phosphorus atom in this adduct would be expected to be downfield of the resonance for monomeric $(Me_3SiCH_2)_2GaPPh_2$ (-27.2ppm) because the phosphorus is bonded to an electron withdrawing Lewis acid, $Ga(CH_2SiMe_3)_3$. The chemical shift of the resonance at -27.4ppm is very similar to that observed for monomeric $(Me_3SiCH_2)_2GaPPh_2$ (-27.2ppm). The line at -35.5 remains unassigned. This line cannot be related to $PPh_2H{\cdot}(Me_3SiCH_2)_2GaPPh_2$ because the ^{31}P NMR spectrum of a mixture of $(Me_3SiCH_2)GaPPh_2$ and PPh_2H has only lines at -27.0 and -40.2ppm, lines due to the two reactants.

The ^1H NMR spectra of R_2MPPh_2 (M = In, CH_2SiMe_3, CH_2CMe_3; Ga, CH_2SiMe_3) consists of an apparent triplet downfield of an intense singlet(s). In the case of $(Me_3CCH_2)_2InPPh_2$, two closely spaced singlets were well resolved but an expanded scale spectrum was required to observe two closely spaced singlets for $(Me_3SiCH_2)_2MPPh_2$ (M=Ga, In). The new line was of significantly lower intensity than the initial singlet. Based on relative intensities the apparent triplet has been assigned to the methylene protons whereas the singlets are due to methyl protons. However, it is not possible to assign lines to the monomer or the dimer or to relate the multiplicity of lines to restricted rotation or to proton-phosphorus coupling. The concentration dependence of the spectra over the range from about 0.1 to 0.5 m were investigated but no definitive changes in the spectra were noticed. Similarly, no significant changes were observed over the temperature range from -45°C to +55°C. It was not even possible for 270 MHz spectra to provide more definitive data. Consequently, no attempt will be made to interpret the currently available data further.

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Table 1. Crystal Data for $[Ph_2PInR_2]_2$ ($R = -CH_2SiMe_3$)

compd	$C_{40}H_{64}In_2P_2Si_4$
mol wt	948.89
space group	$P\bar{1}$
cell constants	
a, Å	10.323(4)
b, Å	11.113(5)
c, Å	21.509(8)
α, deg	83.85(5)
β, deg	86.66(6)
γ, deg	83.27(5)
cell vol, $Å^3$	2433.72
molecules/unit cell(Z)	2
ρ(calcd), gcm-3	1.29
μ(calcd), cm-1	11.23
radiation	Mo K(alpha)
max crystal dimens, mm	0.40x0.30x0.25
scan width, deg	0.8+0.2 tanθ
std reflctns	600, 060, 0016
decay of stds	± 2%
reflctns measd	4389
2(θ) range	2 - 40°
obsd reflctns	3787
no. of parameters varied	433
GOF	1.09
R	0.035
Rw	0.042

Table II

Final Fractional Coordinates for $[(Me_3SiCH_2)_2InPPh_2]_2$

Atom	x/a	y/b	z/c
In(1)	0.92765(5)	0.37788(5)	0.56246(3)
In(2)	0.44974(5)	0.65226(5)	0.94433(3)
P(1)	0.9619(2)	0.6112(2)	0.5528(1)
P(2)	0.5481(2)	0.4254(2)	0.9344(1)
Si(1)	0.6168(2)	0.3707(2)	0.6323(1)
Si(2)	1.1016(2)	0.1209(2)	0.6351(1)
Si(3)	0.6225(3)	0.8333(2)	0.8335(1)
Si(4)	0.1388(3)	0.8056(3)	0.9380(1)
C(1)	0.7207(7)	0.3504(9)	0.5598(4)
C(2)	0.620(1)	0.223(1)	0.6826(5)
C(3)	0.4438(9)	0.421(1)	0.6088(5)
C(4)	0.668(1)	0.491(1)	0.6794(5)
C(5)	1.0710(9)	0.2889(8)	0.6298(4)
C(6)	1.279(1)	0.075(1)	0.6544(7)
C(7)	1.000(1)	0.051(1)	0.7014(6)
C(8)	1.066(2)	0.056(1)	0.5617(6)
C(9)	1.0620(8)	0.6411(7)	0.6156(4)
C(10)	1.0236(9)	0.6077(9)	0.6768(4)
C(11)	1.100(1)	0.632(1)	0.7259(5)
C(12)	1.214(1)	0.688(1)	0.7117(5)
C(13)	1.2524(9)	0.7187(9)	0.6509(5)
C(14)	1.1763(8)	0.6967(8)	0.6012(4)
C(15)	0.8127(8)	0.7143(7)	0.5613(4)
C(16)	0.7073(8)	0.6961(9)	0.5257(4)
C(17)	0.589(1)	0.774(1)	0.5287(6)
C(18)	0.580(1)	0.868(1)	0.5682(7)
C(19)	0.684(1)	0.884(1)	0.6040(6)
C(20)	0.8010(9)	0.8078(8)	0.5999(5)
C(21)	0.5838(8)	0.7907(8)	0.9180(4)
C(22)	0.746(2)	0.717(1)	0.7987(6)
C(23)	0.698(1)	0.983(1)	0.8274(7)
C(24)	0.475(1)	0.857(2)	0.7861(7)
C(25)	0.2440(7)	0.6650(8)	0.9189(5)
C(26)	-0.028(1)	0.762(1)	0.9688(7)
C(27)	0.115(1)	0.912(1)	0.8648(6)
C(28)	0.209(1)	0.888(1)	0.9973(6)
C(29)	0.4466(8)	0.3507(8)	0.8865(4)
C(30)	0.4080(9)	0.408(1)	0.8294(5)
C(31)	0.329(1)	0.348(1)	0.7932(5)
C(32)	0.291(1)	0.236(1)	0.8162(7)
C(33)	0.329(1)	0.182(1)	0.8736(8)
C(34)	0.408(1)	0.238(1)	0.9100(5)
C(35)	0.7113(8)	0.4078(8)	0.8966(5)
C(36)	0.742(1)	0.327(1)	0.8510(5)
C(37)	0.871(2)	0.315(2)	0.8243(5)
C(38)	0.962(2)	0.382(2)	0.846(1)
C(39)	0.934(1)	0.461(1)	0.8910(9)
C(40)	0.8029(9)	0.4761(9)	0.9189(6)

Table III

Bond Lengths (Å) and Bond Angles (deg) for $[(Me_3SiCH_2)_2InPPh_2)_2$

Atoms	Distance	Distance
In -- P	2.643(2)	2.632(2)
In -- P′	2.664(2)	2.659(2)
In -- C(1)	2.198(7)	2.196(8)
In -- C(5)	2.206(8)	2.209(8)
P -- C(9)	1.829(8)	1.832(9)
P -- C(15)	1.821(8)	1.826(8)
Si(1) -- C(1)	1.860(8)	1.861(9)
Si(1) -- C(2)	1.86(1)	1.89(1)
Si(1) -- C(3)	1.89(1)	1.91(1)
Si(1) -- C(4)	1.90(1)	1.86(1)
Si(2) -- C(5)	1.848(9)	1.864(9)
Si(2) -- C(6)	1.90(1)	1.91(1)
Si(2) -- C(7)	1.87(1)	1.88(1)
Si(2) -- C(8)	1.87(1)	1.87(1)
C(9) -- C(10)	1.38(1)	1.38(1)
C(9) -- C(14)	1.40(1)	1.39(1)
C(10) -- C(11)	1.42(1)	1.43(1)
C(11) -- C(12)	1.40(1)	1.37(2)
C(12) -- C(13)	1.36(1)	1.38(2)
C(13) -- C(14)	1.42(1)	1.40(2)
C(15) -- C(16)	1.41(1)	1.40(1)
C(15) -- C(20)	1.39(1)	1.41(1)
C(16) -- C(17)	1.41(1)	1.42(2)
C(17) -- C(18)	1.41(2)	1.40(2)
C(18) -- C(19)	1.40(2)	1.37(2)
C(19) -- C(20)	1.39(1)	1.45(2)

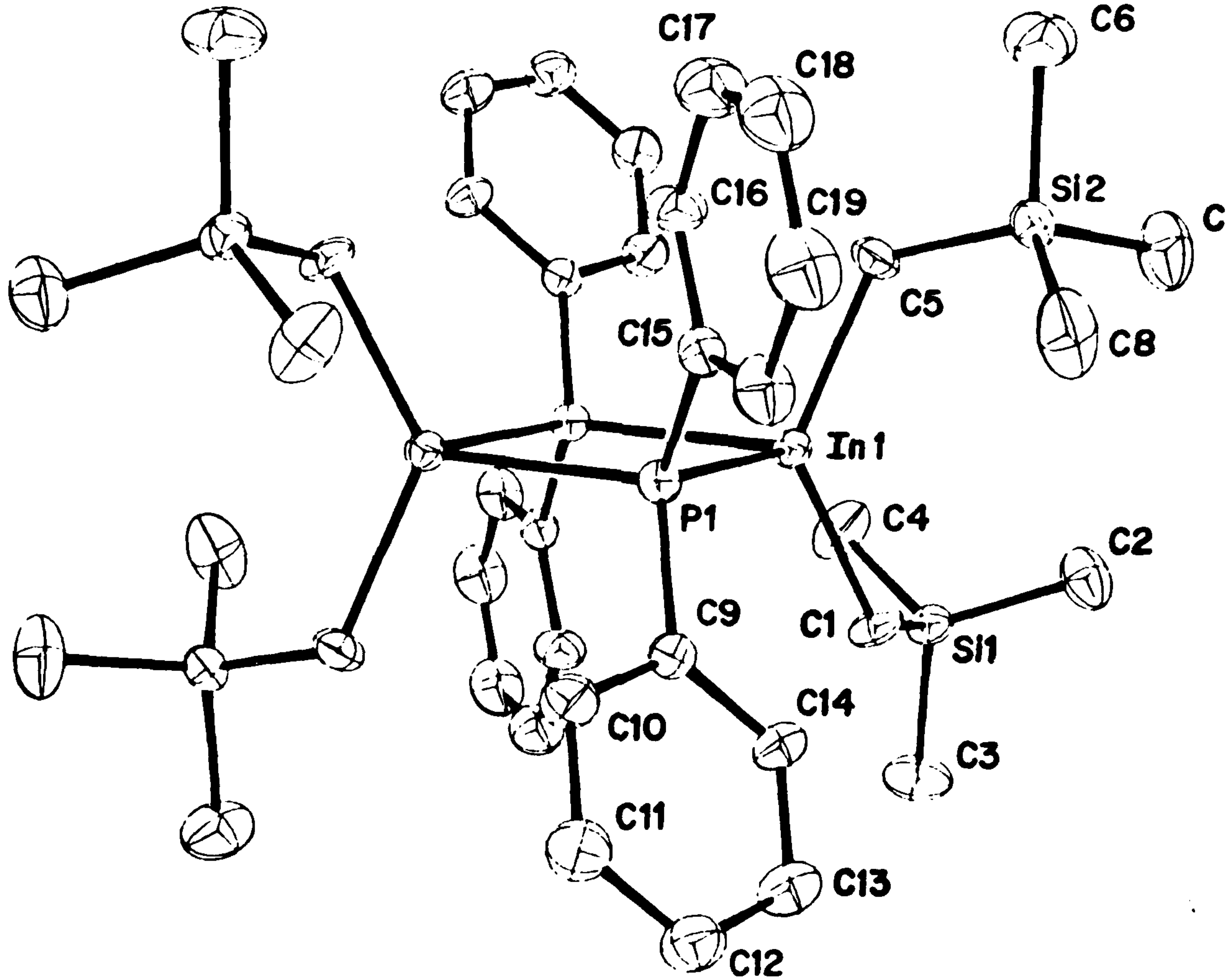
Atoms			Angle	Angle
P	-- In	-- P'	83.23(7)	81.80(7)
P	-- In	-- C(1)	112.1(3)	115.7(2)
P'	-- In	-- C(1)	110.1(2)	112.3(2)
P	-- In	-- C(5)	104.9(2)	106.1(2)
P'	-- In	-- C(5)	109.6(2)	106.0(2)
C(1)	-- In	-- C(5)	127.8(3)	125.9(3)
In	-- P	-- In'	96.77(7)	98.20(8)
In	-- P	-- C(9)	110.0(3)	110.8(3)
In'	-- P	-- C(9)	116.9(3)	116.6(3)
In	-- P	-- C(15)	114.8(3)	114.8(3)
In'	-- P	-- C(15)	114.4(3)	111.8(3)
C(9)	-- P	-- C(15)	104.3(4)	105.0(4)
C(1)	-- Si(1)	-- C(2)	109.8(5)	112.1(5)
C(1)	-- Si(1)	-- C(3)	108.0(4)	107.1(5)
C(2)	-- Si(1)	-- C(3)	109.0(5)	107.8(7)
C(1)	-- Si(1)	-- C(4)	113.2(4)	112.6(5)
C(2)	-- Si(1)	-- C(4)	109.1(6)	108.7(8)
C(3)	-- Si(1)	-- C(4)	107.6(6)	108.3(8)
C(5)	-- Si(2)	-- C(6)	108.2(5)	108.7(5)
C(5)	-- Si(2)	-- C(7)	110.5(5)	109.4(5)
C(6)	-- Si(2)	-- C(7)	106.4(6)	107.8(6)
C(5)	-- Si(2)	-- C(8)	113.4(5)	113.3(4)
C(6)	-- Si(2)	-- C(8)	109.9(7)	109.2(7)
C(7)	-- Si(2)	-- C(8)	108.2(6)	108.3(6)
In	-- C(1)	-- Si(1)	117.3(4)	118.9(4)
In	-- C(5)	-- Si(2)	117.0(4)	115.8(4)
P	-- C(9)	-- C(10)	119.1(6)	119.5(7)
P	-- C(9)	-- C(14)	120.0(6)	118.5(8)
C(10)	-- C(9)	-- C(14)	120.9(8)	122.0(9)
C(9)	-- C(10)	-- C(11)	119.4(9)	118(1)
C(10)	-- C(11)	-- C(12)	120(1)	120(1)
C(11)	-- C(12)	-- C(13)	120.0(9)	121(1)
C(12)	-- C(13)	-- C(14)	120.9(9)	121(1)
C(9)	-- C(14)	-- C(13)	118.9(9)	118(1)
P	-- C(15)	-- C(16)	116.7(6)	120.9(8)
P	-- C(15)	-- C(20)	122.8(7)	115.4(8)
C(16)	-- C(15)	-- C(20)	120.5(8)	123.6(9)
C(15)	-- C(16)	-- C(17)	120.0(9)	119(1)
C(16)	-- C(17)	-- C(18)	118(1)	118(2)
C(17)	-- C(18)	-- C(19)	121(1)	124(2)
C(18)	-- C(19)	-- C(20)	120(1)	119(2)
C(15)	-- C(20)	-- C(19)	120(1)	117(1)

Table II

Figures

Figure 1. Labeling of atoms in $[(Me_3SiCH_2)_2InPPh_2]_2$ (Molecule A) Ortep-II diagram showing 30% probability contours of the thermal vibration ellipsoids of non-hydrogen atoms.

Figure 2. Stereoscopic view of the unit cell of $[(Me_3SiCH_2)_2InPPh_2]_2$.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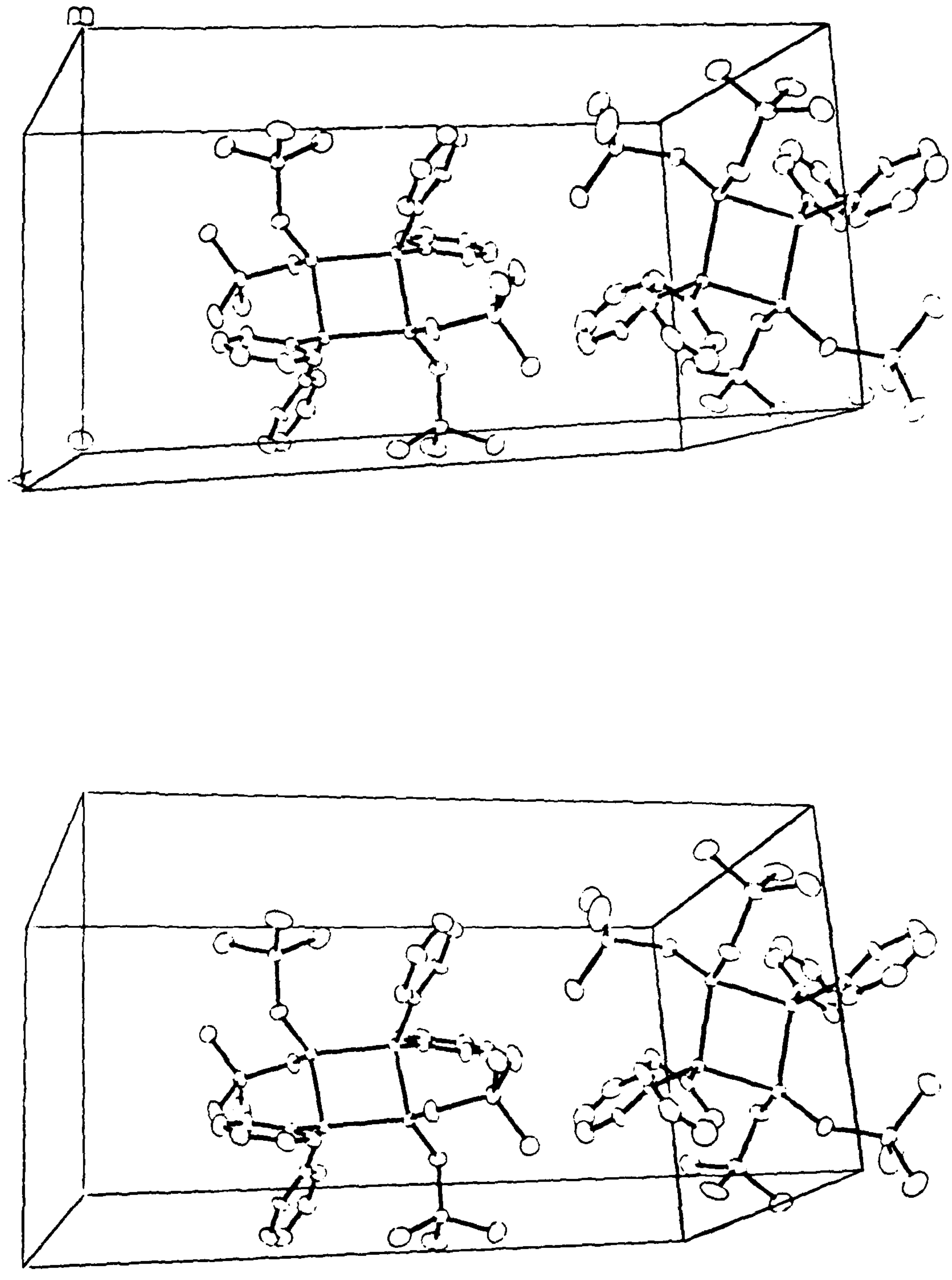
C13
C12



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