3036 *Organometallics* 1991, *10*, 3036-3040

Methylene-Bridged Group 13–15 Compounds, $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In). Crystal Structure of $[(Me_3CCH_2)_2InCH_2PPh_2]_2{\cdot}C_6D_6$, a Molecule Containing an In–C–P–In–C–P Ring in a Chair Conformation

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Received February 22, 1991

A series of compounds of the type $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In) has been prepared by metathetical reactions between the appropriate diorganometal halide and $LiCH_2PPh_2$ in pentane or Et_2O at −78 °C. All compounds were characterized by physical properties, partial elemental analyses (C, H), and cryoscopic molecular weight measurements in benzene solution as well as IR, ^1H NMR, and ^{31}P NMR spectroscopic data. All appropriate data support the existence of dimeric molecules. The monomeric species dimerize by apparent Lewis acid–base interactions. These interactions are sufficiently strong that the compounds do not form stable adducts with oxygen- or nitrogen-containing Lewis bases. $[(Me_3CCH_2)_2InCH_2PPh_2]_2{\cdot}C_6D_6$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with a = 13.142 (3) Å, b = 15.109 (3) Å, c = 15.746 (4) Å, α = 85.27 (2)°, β = 67.99 (2)°, γ = 66.00 (1)°, V = 2639 (1) Å^3, and Z = 2. Diffraction data (Mo Kα, 2θ = 4.5–45.0°) were collected on a Syntex $P2_1$ diffractometer; the structure was solved and refined to R_F = 6.0% and R_{wF} = 6.4% for all 6932 independent reflections (R_F = 4.5% and R_{wF} = 6.2% for those 5495 data with $|F_o| > 6\sigma(|F_o|)$). The crystal is composed of two crystallographically independent $[(Me_3CCH_2)InCH_2PPh_2]_2$ molecules (each having precise C_i symmetry) and a C_6D_6 molecule of solvation. The two independent $[(Me_3CCH_2)InCH_2PPh_2]_2$ molecules have similar configurations. Each is based upon a six-membered In–CH_2–P–In–CH_2–P ring with a chair conformation. Bond lengths of interest include In–P = 2.694 (2)–2.703 (2) Å, In–CH_2 = 2.255 (7)–2.261 (8) Å, and In–neopentyl = 2.216 (7)–2.234 (7) Å.

Introduction

Single-source precursors of the types $R_3MER'_3$[1] and $R_2MER'_2$[2] (M = group 13 element, E = group 15 element) have been used to prepare group 13–15 materials such as GaAs and InP. An alternative class of potential precursors that contain only the group 13 and 15 elements, carbon, and hydrogen are compounds of the type $R_2MCH_2ER'_2$. This class of compounds has a methylene group that bridges the group 13 and 15 elements in order to establish as well as to fix the group 13/15 ratio at 1 as required for the desired material. Thus, compounds of this type incorporate simple Lewis acid and base sites without the possibility of π bonding in the monomeric species between the vacant orbital on the group 13 element and the electron pair on the group 15 element. The only reported heavier 13–CH_2–15 species are aluminum compounds including $Cl_{3-x}Al(CH_2PMe_2)_x$,[3] $Me_{3-x}Al(CH_2PMe_2)_x$ (x = 1–3),[3,4,5] and $LiAl(CH_2PMe_2)_4$.[5]

In this paper, we report the synthesis and characterization of $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In). All compounds were characterized by elemental analyses (C, H), physical properties, and cryoscopic molecular weight studies in benzene as well as IR, ^1H NMR, and ^{31}P NMR spectral data. In addition, an X-ray structural study was used to investigate the crystalline state of $(Me_3CCH_2)_2InCH_2PPh_2$.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The compounds $Ga(CH_2CMe_3)_2Cl$,[6] $In(CH_2CMe_3)_2Cl$,[7] $Ga(CH_2SiMe_3)_2Cl$,[6] $In(CH_2SiMe_3)_2Cl$,[8] $LiCH_2PPh_2$,[9] and Li(TMEDA)CH_2PPh_2[10] were prepared and purified by literature methods. Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. 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), vw (very weak), and sh (shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. 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. All samples for NMR spectra were contained in sealed NMR tubes. 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.[11]

Synthesis of $(Me_3CCH_2)_2GaCH_2PPh_2$. A 100-mL round-bottom two-neck flask was charged with 1.467 g (5.929 mmol) of $Ga(CH_2CMe_3)_2Cl$ and fitted with a side-arm dumper containing 1.188 g (5.968 mmol) of $LiCH_2PPh_2$. After the organogallium reagent was dissolved in 40 mL of pentane and cooled to −78 °C, $LiCH_2PPh_2$ was slowly added to the mixture with stirring for 15 min. The mixture was allowed to warm to ambient temperature on its own accord and stirred for 18 h. The colorless solid remaining after the pentane was removed was extracted six times with a benzene/pentane mixture (45/20 mL) and finally recrystallized from benzene to give 1.910 g (4.644 mmol) of

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$(Me_3CCH_2)_2GaCH_2PPh_2$ in 87.6% yield based on $Ga(CH_2CMe_3)_2Cl$. Mp: crystals became opaque with rounded edges at 178–183 °C and then melted at 187–188 °C. ^1H NMR (C_6H_6, δ): 0.62 (d, $^3J_{PGaCH}$ = 3.6 Hz, 4 H, CH_2Ga), 1.03 (s, 18 H, CMe_3), 1.63 (dd, $^2J_{PCH}$ = 11.7 Hz, $^3J_{PGaCH}$ = 8.1 Hz, 2 H, CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −10.1 (s). $^{31}P\{^1H\}$ NMR (d^8-THF, δ) −9.96 (s). Anal. Calcd for $[(Me_3CCH_2)_2GaCH_2PPh_2]\cdot 0.75C_6H_6$: C, 70.29; H, 8.28. Found: C, 70.23; H, 8.58. (The compound $(Me_3CCH_2)_2GaCH_2PPh_2$ was crystallized from benzene solution.) IR (Nujol mull, cm^{-1}): 3085 (vw), 3070 (w), 3050 (vw), 3018 (vw), 1809 (vw, br), 1585 (vw), 1570 (vw), 1355 (m), 1305 (vw), 1224 (vw), 1182 (vw), 1155 (vw), 1135 (vw), 1095 (w), 1070 (w), 1024 (w), 995 (w), 785 (w), 772 (w), 745 (m), 738 (s), 718 (sh), 710 (m), 701 (sh), 693 (s), 640 (w), 620 (w), 560 (w), 534 (w), 505 (w), 474 (w).

Synthesis of $(Me_3CCH_2)_2InCH_2PPh_2$. The compound $(Me_3CCH_2)_2InCH_2PPh_2$ (1.291 g, 2.828 mmol, 92.3% yield) was prepared from 0.897 g (3.07 mmol) of $In(CH_2CMe_3)_2Cl$ and 0.635 g (3.08 mmol) $LiCH_2PPh_2$ in pentane by using the procedure previously described. Crystals of $(Me_3CCH_2)_2InCH_2PPh_2$ suitable for an X-ray structural study were obtained from a saturated d_6-benzene solution at ambient temperature. Mp: 205.5–209.5 °C. ^1H NMR (C_6H_6, δ): 0.70 (d, $^3J_{PInCH}$ = 8.6 Hz, 4 H, CH_2In), 0.90 (s, 18 H, CMe_3), 1.46 (dd, $^2J_{PCH}$ = 9.9 Hz, $^3J_{PInCH}$ = 4.5 Hz, 2 H, CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −8.41 (s). Cryoscopic molecular weight, formula weight 456.47 (calculated molality, observed molality, association): 0.0640, 0.0327, 1.96. Anal. Calcd for $(Me_3CCH_2)_2InCH_2PPh_2$: C, 60.52; H, 7.51. Found: C, 60.58; H, 7.68. IR (Nujol mull, cm^{-1}): 3080 (vw), 3058 (vw), 1870 (vw), 1803 (vw), 1581 (vw), 1569 (vw), 1478 (sh, m), 1431 (vs), 1355 (s), 1330 (w), 1324 (w), 1299 (w), 1275 (w), 1230 (m), 1210 (w), 1180 (vw), 1165 (vw), 1110 (w), 1094 (w), 1085 (vw, sh), 1065 (vw), 1022 (vw), 1008 (w), 995 (w), 988 (w), 962 (vw), 945 (m), 910 (vw), 838 (vw), 768 (m), 740 (m), 732 (s), 717 (m), 699 (m, sh), 689 (vs), 674 (m), 668 (m), 608 (m), 561 (w), 516 (m), 488 (vw), 460 (vw), 445 (vw), 338 (vw).

Synthesis of $(Me_3SiCH_2)_2GaCH_2PPh_2$. The compound $(Me_3SiCH_2)_2GaCH_2PPh_2$ (2.118 g, 4.778 mmol, 94.5% yield based on $Ga(CH_2CMe_3)_2Cl$) was prepared from 1.413 g (5.052 mmol) of $Ga(CH_2SiMe_3)_2Cl$ and $LiCH_2PPh_2$ (1.058 g, 5.133 mmol) by using the procedure previously described. Crystals were obtained from a saturated benzene solution at ambient temperature. Mp: crystals appeared glassy at 180 °C and melted at 207–212 °C. ^1H NMR (C_6H_6, δ): −0.61 (d, $^3J_{PGaCH}$ = 4.2 Hz, 4 H, CH_2Ga), 0.11 (s, 18 H, $SiMe_3$), 1.62 (dd, $^2J_{PCH}$ = 10.8 Hz, $^3J_{PGaCH}$ = 7.2 Hz, 2 H, CH_2P). $^{13}C\{^1H\}$ NMR (C_6D_6, 0.21 M, δ): −0.16 (dd, $^2J_{PCGaC}$ = 7.4 Hz, $^3J_{PGaC}$ = 3.7 Hz, CH_2P), 3.31 (s, $SiMe_3$), 7.48 (dd, J_{PC} = 18.3 Hz, $^2J_{PGaC}$ = 6.1 Hz, CH_2P). $^{29}Si\{^1H\}$ NMR (C_6D_6, δ): 17.7 (s). $^{31}P\{^1H\}$ (C_6D_6, δ): −10.2 (s). Anal. Calcd for $(Me_3SiCH_2)_2GaCH_2PPh_2$: C, 56.88; H, 7.73; P, 6.99. Found: C, 57.02; H, 7.62; P, 6.50. Cryoscopic molecular weight, formula weight 443.37 (calculated molality, observed molality, association): 0.136, 0.0691, 1.98; 0.0911, 0.0452, 2.02; 0.0631, 0.0326, 1.94. IR (Nujol mull, cm^{-1}): 3080 (w), 3060 (w), 1735 (vw, br), 1586 (w), 1570 (w), 1330 (w), 1303 (w), 1255 (s), 1240 (s), 1185 (w), 1097 (m), 1070 (w), 1028 (m), 1005 (s), 998 (s), 978 (s), 967 (m), 910 (w), 853 (s), 821 (s), 770 (m), 750 (m, sh), 737 (s), 723 (s), 703 (m), 692 (s), 678 (m), 635 (s), 612 (w), 588 (w), 552 (s), 520 (m), 510 (m), 495 (w), 474 (m), 430 (w), 347 (w).

Synthesis of $(Me_3SiCH_2)_2InCH_2PPh_2$. The compound $(Me_3SiCH_2)_2InCH_2PPh_2$ was synthesized from $In(CH_2SiMe_3)_2Cl$ and $LiCH_2PPh_2$ or $Li(TMEDA)CH_2PPh_2$ in pentane or diethyl ether, respectively, by using the procedure previously described. The product was isolated in 92.4% yield when $LiCH_2PPh_2/C_5H_{12}$ were used, whereas only a 79.4% yield was obtained from $Li(TMEDA)CH_2PPh_2/OEt_2$. Crystals were grown after slow diffusion of anhydrous pentane into a benzene solution of the compound. All properties of the two products were identical. Mp: 208–210 °C. ^1H NMR (C_6H_6, δ): −0.57 (d, $^3J_{PInCH}$ = 3.6 Hz, 4 H, CH_2In), 0.14 (s, 18 H, $SiMe_3$), 1.50 (dd, $^2J_{PCH}$ = 10.8 Hz, $^3J_{PInCH}$ = 4.5 Hz, 2 H, CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −10.0 (s). Cryoscopic molecular weight, formula weight 488.47 (calculated molality, observed molality, association): 0.127, 0.0726, 1.75; 0.114, 0.0679, 1.67; 0.0735, 0.0414, 1.78; 0.0938, 0.0564, 1.66; 0.0600, 0.0347, 1.75. Anal. Calcd for $(Me_3SiCH_2)_2InCH_2PPh_2$: C, 51.64; H, 7.22. Found: C, 51.71; H, 7.27. IR (Nujol mull, cm^{-1}): 3070 (w), 3060 (w), 3050 (w), 1802 (vw), 1582 (vw), 1570 (vw), 1478 (m), 1431 (s), 1350 (w), 1324 (w), 1298 (w), 1252 (w, sh), 1238 (s), 1159 (vw), 1152 (vw), 1110 (vw), 1100 (vw), 1095 (w, sh), 1085 (w), 1065 (w), 1023 (w), 995 (w), 990 (vw), 965 (m, sh), 960 (m), 952 (m), 940 (m), 928 (m), 912 (w, sh), 854 (s), 838 (m), 820 (vs), 769 (m), 748 (m, sh), 742 (vs), 732 (vs), 720 (s), 700 (m), 688 (vs), 678 (m, sh), 616 (m), 562 (w), 550 (w), 518 (m), 490 (m), 482 (m), 462 (m), 390 (vw), 338 (vw).

Lewis Acid–Base Studies of $R_2MCH_2PPh_2$ Compounds (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In). Proton NMR spectroscopy was used to investigate the Lewis acidity of $R_2MCH_2PPh_2$. A reaction tube equipped with an NMR tube as a side arm was charged with a weighed amount of the desired compound. The tube was fitted with an adapter and evacuated. The appropriate base (in excess) was distilled into the tube. The mixture was allowed to stir 15–18 h at ambient temperature. The base was removed by vacuum distillation and the solid remaining in the tube was evacuated for 15 h. Five milliliters of benzene was distilled into the reaction tube and an aliquot (ca. 0.7 mL) of the resulting solution was decanted into the NMR tube. The mixture in the NMR tube was frozen at −196 °C, and the tube was then flame-sealed.

No stable room-temperature Lewis acid–base adducts, $(Me_3SiCH_2)_2GaCH_2PPh_2\cdot L$, were observed for L = Et_2O, THF, DME (dimethoxyethane), MeCN, NMe_3, and TMEDA. Similar studies with $(Me_3YCH_2)_2MCH_2PPh_2$, where Y = Si, C, M = Ga, In, revealed no adducts for L = Et_2O, THF, and TMEDA.

The compound $(Me_3SiCH_2)_2GaCH_2PPh_2$ does form an apparent adduct with excess NMe_3 in benzene solution. A sample of the compound was reacted with a 4-fold excess of NMe_3 in protic benzene and poured into an NMR tube. ^1H NMR (C_6H_6, δ): −0.81 (s, 1 H, CH_2), 0.14 (s, 6 H, $SiMe_3/CH_2$), 2.05 (s, NMe_3).

Collection of X-ray Diffraction Data for $[(Me_3CCH_2)_2InCH_2PPh_2]_2\cdot C_6D_6$. A colorless crystal of approximate orthogonal dimensions 0.3 × 0.3 × 0.4 mm, and rather "cubelike" in shape, was mounted in a thin-walled glass capillary under a carefully purified argon atmosphere. The crystal was aligned and centered on a Syntex $P2_1$ automated four-circle diffractometer. Determinations of accurate cell dimensions, the orientation matrix, and Laue symmetry were carried out as described previously.[12] Details of this and data collection are provided in Table I.

A survey of the data set revealed no systematic absences and no symmetry other than the Friedel condition. The crystal thus belongs to the triclinic class, possible space groups being the centrosymmetric $P\bar{1}$ (C_i^1; No. 2) or the noncentrosymmetric $P1$ (C_1^1; No. 2). The former, centrosymmetric, alternative was adjudged the most probably based upon cell content and intensity statistics; this was confirmed by the successful solution of the structure in the higher symmetry space group.

All data were corrected for the effects of absorption, and symmetry equivalent reflections were averaged; the resulting unique data were corrected for Lorentz and polarization effects, were converted to unscaled $|F_o|$ values, and were placed on an approximately absolute scale by means of a Wilson plot. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$ and was retained in the data set.

Solution and Refinement of the Structure of $[(Me_3CCH_2)_2InCH_2PPh_2]_2\cdot C_6H_6$. All calculations were performed on our locally modified set of Syntex XTL computer programs. The calculated structure factors were based on the analytical form of the scattering factors for neutral atoms;[13a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[13b] were included for all atoms. The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}$.

The positions of the indium atoms (Z = 49) were determined from a Patterson map. There are two independent indium atoms in the asymmetric unit. In(1) and In(1)* define the core of a dimeric molecule centered about the inversion center at $^1/_2$, $^1/_2$, $^1/_2$ while In(2) and In(2)* define the core of a second molecule centered about $^1/_2$, 0, 0. A difference-Fourier synthesis (R_F =

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Table I. Experimental Data for the X-ray Diffraction Study of $[(Me_3CCH_2)_2InCH_2PPh_2]_2 \bullet C_6D_6$

(A) Unit Cell Parameters at 24 °C (297 K)

crystal system: triclinic
a = 13.142 (3) Å
b = 15.109 (3) Å
c = 15.746 (4) Å
α = 85.27 (2)°
β = 67.99 (2)°
γ = 66.00 (1)°

space group: $P\bar{1}$ (C_i^1; No. 2)
V = 2639 (1) Å^3
formula: $C_{46}H_{68}In_2P_2 \cdot C_6D_6$
fw: 912.5 + 84.1
Z = 2
D(calcd) = 1.25 g cm^{-3}

(B) Data Collection

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: pyrolytic graphite in equatorial geometry ($2\theta_m$ = 12.2°, assumed to be 50% perfect/50% ideally mosaic for polarization correction)
reflns measd: $h,\pm k,\pm l$ for 2θ = 4.5–45.0° ($h = 0 \rightarrow 14$, $k = -14 \rightarrow +16$, $l = -15 \rightarrow +16$); 7523 data were merged to 6932 independent reflns ($R(I)$ = 1.5% and $R(wI)$ = 1.7% for averaged pairs)
scan type: coupled θ(crystal)–2θ(counter) scan at 4.0 deg/min in 2θ over the range [2θ(Mo Kα_1) − 0.9]° through [2θ(Mo Kα_2) + 0.9]°
background measurement: stationary cryst and counter at each extreme of the 2θ scan; each for one-half total scan time
std reflns: 3 (184, $2\bar{3}\bar{8}$, $1\bar{8}\bar{2}$) remeasd after each batch of 97 reflns; no significant fluctuations nor decay was obsd

Absorption Corrections[a]
234, 14.82°, 1.121
346, 18.25°, 1.132
358, 24.20°, 1.112
569, 27.57°, 1.136
689, 30.95°, 1.146

[a] Data were corrected by interpolation in 2θ and ϕ between the normalized transmission curves of ψ scans of five close-to-axial reflections; their *hkl* indices, 2θ values, and maximum/minimum intensities are tabulated.

Table II. Final Atomic Coordinates for $[(Me_3CCH_2)_2InPPh_2CH_2]_2 \bullet C_6D_6$

atom	x	y	z
	(A) Molecule 1		
In(1)	0.356 66 (4)	0.450 45 (3)	0.598 34 (3)
P(1)	0.362 55 (15)	0.550 47 (12)	0.448 02 (11)
C(1)	0.488 50 (54)	0.480 17 (50)	0.638 65 (43)
C(11)	0.166 42 (59)	0.527 23 (54)	0.693 11 (48)
C(12)	0.135 83 (60)	0.552 21 (53)	0.795 11 (46)
C(13)	0.192 49 (88)	0.458 72 (73)	0.838 86 (62)
C(14)	−0.002 42 (67)	0.595 30 (73)	0.845 71 (56)
C(15)	0.181 86 (86)	0.627 19 (72)	0.805 27 (67)
C(21)	0.423 41 (70)	0.307 32 (51)	0.524 32 (52)
C(22)	0.404 67 (75)	0.224 15 (53)	0.578 08 (53)
C(23)	0.475 51 (94)	0.128 37 (59)	0.518 46 (65)
C(24)	0.461 8 (10)	0.212 01 (68)	0.655 89 (66)
C(25)	0.276 8 (10)	0.240 43 (78)	0.628 83 (92)
C(31)	0.274 61 (59)	0.524 47 (43)	0.393 78 (44)
C(32)	0.148 66 (60)	0.560 80 (55)	0.440 22 (51)
C(33)	0.080 08 (71)	0.540 56 (64)	0.401 81 (65)
C(34)	0.134 95 (84)	0.482 58 (64)	0.319 12 (68)
C(35)	0.260 91 (84)	0.446 09 (59)	0.272 70 (61)
C(36)	0.331 51 (63)	0.468 18 (49)	0.310 53 (51)
C(41)	0.286 56 (54)	0.682 66 (44)	0.469 09 (45)
C(42)	0.251 84 (73)	0.739 64 (51)	0.401 43 (57)
C(43)	0.187 80 (90)	0.842 92 (61)	0.423 61 (77)
C(44)	0.165 12 (76)	0.885 61 (55)	0.505 00 (70)
C(45)	0.199 54 (77)	0.827 73 (58)	0.571 05 (61)
C(46)	0.259 40 (66)	0.727 06 (51)	0.553 20 (51)
	(B) Molecule 2		
In(2)	0.452 12 (4)	0.085 03 (3)	0.135 16 (3)
P(2)	0.421 84 (14)	0.145 07 (12)	−0.023 59 (11)
C(2)	0.463 74 (54)	−0.067 07 (45)	0.125 40 (45)
C(51)	0.280 05 (60)	0.186 28 (48)	0.240 20 (44)
C(52)	0.210 30 (60)	0.146 22 (47)	0.325 57 (43)
C(53)	0.108 88 (75)	0.234 29 (63)	0.392 85 (56)
C(54)	0.295 82 (83)	0.078 43 (69)	0.373 40 (57)
C(55)	0.154 30 (78)	0.087 19 (66)	0.298 64 (61)
C(61)	0.625 13 (70)	0.097 09 (66)	0.100 07 (54)
C(62)	0.654 50 (68)	0.135 75 (63)	0.167 64 (62)
C(63)	0.654 0 (16)	0.056 9 (18)	0.243 74 (93)
C(64)	0.782 28 (76)	0.128 52 (76)	0.130 82 (70)
C(65)	0.568 0 (11)	0.226 9 (11)	0.219 6 (15)
C(71)	0.275 72 (57)	0.162 60 (44)	−0.026 10 (46)
C(72)	0.200 87 (56)	0.128 75 (51)	0.043 88 (50)
C(73)	0.092 22 (64)	0.139 34 (54)	0.041 75 (55)
C(74)	0.056 14 (70)	0.182 91 (60)	−0.029 35 (59)
C(75)	0.130 26 (79)	0.217 86 (66)	−0.096 94 (61)
C(76)	0.242 23 (65)	0.207 72 (53)	−0.096 69 (49)
C(81)	0.421 27 (55)	0.267 52 (44)	−0.038 96 (42)
C(82)	0.511 76 (68)	0.284 44 (51)	−0.110 62 (53)
C(83)	0.510 92 (76)	0.377 55 (55)	−0.117 38 (59)
C(84)	0.421 38 (91)	0.452 37 (63)	−0.053 95 (67)
C(85)	0.329 49 (82)	0.436 98 (51)	0.017 92 (59)
C(86)	0.328 69 (67)	0.344 12 (49)	0.025 08 (50)
	(C) C_6D_6 of Solvation		
C(91)	0.030 1 (10)	0.123 2 (12)	0.704 57 (81)
C(92)	−0.027 4 (15)	0.227 7 (12)	0.716 9 (12)
C(93)	−0.127 5 (12)	0.269 62 (94)	0.788 6 (11)
C(94)	−0.175 0 (10)	0.214 0 (11)	0.852 14 (86)
C(95)	−0.115 7 (12)	0.114 1 (10)	0.837 78 (87)
C(96)	−0.018 4 (11)	0.068 00 (93)	0.767 51 (88)

40.6%)[14] revealed the positions of the 2 independent phosphorus atoms and 37 of the carbon atoms. All remaining carbon atoms (including six from a molecule of solvation, C_6D_6, lying in a general position) were located from a second difference-Fourier synthesis. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with R_F = 6.0%, R_{wF} = 6.4%, and GOF = 2.42 for 505 variables refined against all 6932 independent reflections. Discrepancy indices for those 6021 data with $|F_o| > 3\sigma(|F_o|)$ were R_F = 5.0% and R_{wF} = 6.3%; for those 5495 data with $|F_o| > 6\sigma(|F_o|)$, these were further reduced to R_F = 4.5% and R_{wF} = 6.2%.

Contributions from all hydrogen atoms except for those on methyl groups of the neopentyl ligands were included in calculated positions with d(C–H) = 0.95 Å.[15] (Methyl hydrogens were omitted because of limited computer memory.)

A final difference-Fourier synthesis showed no unexpected features, and an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of Miller indices, $|F_o|$, $(\sin\theta)/\lambda$, and sequence number showed no unusual trends. The structure is thus correct and complete and the weighting scheme satisfactory. Final atomic coordinates are collected in Table II.

Results and Discussion

A series of compounds of the general type $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In) have been prepared and have been fully characterized. The characterization data include partial elemental analyses (C, H), physical properties, and cryoscopic molecular weight measurements in benzene solution as well as IR, ^{1}H NMR, and ^{31}P NMR spectroscopic data. In addition, a single-crystal X-ray structural study was used to define the nature of $(Me_3CCH_2)_2InCH_2PPh_2$ in the solid state. All compounds were prepared in high yield, typically greater than 90%, by using a metathetical reaction as summarized by the following equation:

$$R_2MCl + LiCH_2PPh_2 \xrightarrow[-78\ ^\circ C]{C_6H_{12}} R_2MCH_2PPh_2 + LiCl(s)$$

$$R = CH_2CMe_3,\ CH_2SiMe_3; \qquad M = Ga,\ In$$

When the reagents were combined in the presence of pentane at −78 °C and then the reaction mixture was warmed to room temperature, high yields of products were obtained. If the reagents were mixed at room temperature, low yields of products, which were gray, were observed.

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[14] $R_F(\%) = 100(\sum||F_o| - |F_c||/\sum|F_o|)$; $R_{wF}(\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

[15] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table III. Selected Interatomic Distances (Å) for $[(Me_3CCH_2)_2InCH_2PPh_2]_2 \bullet C_6D_6$

molecule 1		molecule 2	
(A) Indium-Ligand and P-CH_2 Distances			
In(1)-P(1)	2.694 (2)	In(2)-P(2)	2.703 (2)
In(1)-C(1)	2.261 (8)	In(2)-C(2)	2.255 (7)
In(1)-C(11)	2.226 (8)	In(2)-C(51)	2.234 (7)
In(1)-C(21)	2.216 (7)	In(2)-C(61)	2.211 (10)
P(1)-C(1)[a]	1.809 (7)	P(2)-C(2)[a]	1.812 (7)
(B) Distances Involving the Neopentyl Ligands			
C(11)-C(12)	1.541 (10)	C(51)-C(52)	1.551 (10)
C(12)-C(13)	1.547 (13)	C(52)-C(53)	1.550 (11)
C(12)-C(14)	1.549 (13)	C(52)-C(54)	1.565 (13)
C(12)-C(15)	1.528 (15)	C(52)-C(55)	1.532 (14)
C(21)-C(22)	1.509 (11)	C(61)-C(62)	1.489 (13)
C(22)-C(23)	1.522 (11)	C(62)-C(63)	1.619 (22)
C(22)-C(24)	1.624 (15)	C(62)-C(64)	1.516 (15)
C(22)-C(25)	1.487 (17)	C(62)-C(65)	1.439 (20)
(C) P-C Distances within the PPh_2 Ligands			
P(1)-C(31)	1.839 (8)	P(2)-C(71)	1.844 (9)
P(1)-C(41)	1.826 (6)	P(2)-C(81)	1.843 (7)

[a] This is the distance between the phosphorus in one asymmetric unit and the carbon in the adjacent unit.

Table IV. Selected Interatomic Angles (deg) for $[(Me_3CCH_2)_2InCH_2PPh_2]_2 \bullet C_6D_6$

molecule 1		molecule 2	
(A) Angles Involving the Core Atoms of the Dimer			
P(1)-In(1)-C(1)	100.76 (19)	P(2)-In(2)-C(2)	99.35 (18)
P(1)-In(1)-C(11)	102.06 (21)	P(2)-In(2)-C(51)	101.94 (19)
P(1)-In(1)-C(21)	94.85 (22)	P(2)-In(2)-C(61)	96.49 (24)
P(1)-C(1)-In(1)[a]	116.94 (35)	P(2)-C(2)-In(2)[a]	114.60 (24)
C(1)-In(1)-C(11)	113.57 (27)	C(2)-In(2)-C(51)	113.57 (26)
C(1)-In(1)-C(21)	116.81 (28)	C(2)-In(2)-C(61)	115.69 (30)
C(11)-In(1)-C(21)	122.13 (30)	C(51)-In(2)-C(61)	123.10 (31)
C(1)-P(1)-In(1)[a]	114.42 (24)	C(2)-P(2)-In(2)[a]	116.86 (35)
(B) Selected Angles Involving the Neopentyl Ligands			
In(1)-C(11)-C(12)	120.42 (52)	In(2)-C(51)-C(52)	120.07 (48)
In(1)-C(21)-C(22)	119.35 (57)	In(2)-C(61)-C(62)	122.76 (64)
(C) Angles Involving the Phosphide Ligands			
In(1)-P(1)-C(31)	108.66 (23)	In(2)-P(2)-C(71)	114.90 (24)
In(1)-P(1)-C(41)	115.92 (23)	In(2)-P(2)-C(81)	109.06 (23)
C(1)-P(1)-C(31)[a]	106.92 (33)	C(2)-P(2)-C(71)[a]	106.58 (33)
C(1)-P(1)-C(41)[a]	108.31 (31)	C(2)-P(2)-C(81)[a]	107.81 (32)
C(31)-P(1)-C(41)	101.48 (32)	C(71)-P(2)-C(81)	103.08 (32)
P(1)-C(31)-C(32)	118.25 (55)	P(2)-C(71)-C(72)	119.08 (55)
P(1)-C(31)-C(36)	120.57 (56)	P(2)-C(71)-C(76)	120.04 (57)
P(1)-C(41)-C(42)	120.18 (57)	P(2)-C(81)-C(82)	121.64 (55)
P(1)-C(41)-C(46)	120.05 (56)	P(2)-C(81)-C(86)	118.32 (54)

[a] This is the angle made by atoms in one asymmetric unit with atoms in the adjacent unit.

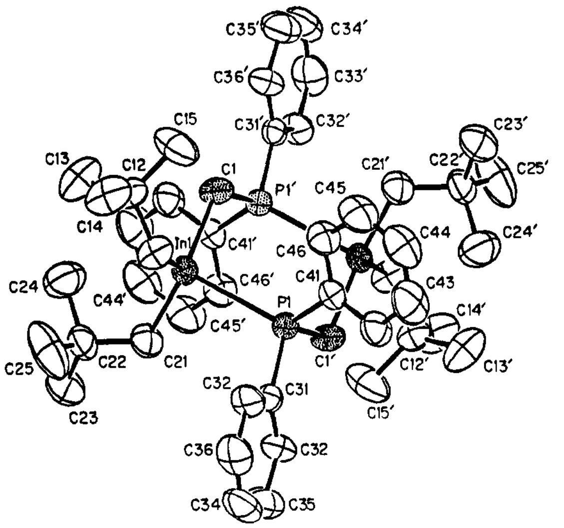

Figure 1. Labeling of atoms for molecule 1 of $[(Me_3CCH_2)_2InCH_2PPh_2]_2$. The P-In-C-P-In-C system has been stippled so as to show clearly its "chair" conformation. Atoms of the basic asymmetric unit have normal labels; those in the other half of the molecule (related to the basic unit by the transformation $1 - x, 1 - y, 1 - z$) are labeled with a prime. All hydrogen atoms are omitted. [ORTEP diagram; 30% probability ellipsoids.]

The gray suggests decomposition of the organometallic species.

Crystals of bis(neopentyl)[(diphenylphosphino)methyl]indium(III) are composed to two independent molecules of composition $[(Me_3CCH_2)_2InCH_2PPh_2]_2$ (each of which lies on a crystallographic inversion center—molecule 1 about $^1/_2$, $^1/_2$, $^1/_2$ and molecule 2 about $^1/_2$, 0, 0) and a C_6D_6 molecule of solvation in a general position. The molecular units are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Distances and angles are provided in Tables III and IV. The two independent $[(Me_3CCH_2)_2InCH_2PPh_2]_2$ molecules have similar configurations. The labeling for molecule 1 is shown in Figure 1.

Subsequent discussion will focus on dimensions in molecule 1, with equivalent dimensions for molecule 2 given in square brackets. Equivalent values for the two molecules appear side by side in Tables III and IV. The system P(1)-In(1)-C(1)-P(1′)-In(1′)-C(1′) [P(2)-In(2)-C(2)-P(2′)-In(2′)-C(2′)] defines a six-membered ring with a "chair" conformation; the In-P···In′-P′ moiety is planar with C(1) and C(1′) [C(2) and C(2′)] lying above and below this plane, respectively. (The possible "boat" conformation is disfavored since it would lead to substantial interaction between CH_2CMe_3 groups on indium and Ph groups on phosphorus (see Figure 1)).

Indium-neopentyl bond lengths are In(1)-C(11) = 2.226 (8) Å and In(1)-C(21) = 2.216 (7) Å [In(2)-C(51) = 2.234 (7) Å and In(2)-C(61) = 2.211 (10) Å], the average being In-C(neopentyl) = 2.222 Å. These distances are comparable to those observed in $[(Me_3CCH_2)_2InPPh_2]_3$[16] of 2.182 (6) and 2.210 (7) Å (average 2.196 Å). The intraring In-CH_2 distance is slightly longer with In(1)-C(1) = 2.261 (8) Å [In(2)-C(2) = 2.255 (7) Å], the average value being 2.258 Å.

The indium-phosphorus distances are In(1)-P(1) = 2.694 (2) Å [In(2)-P(2) = 2.703 (2) Å], average 2.699 Å. The difference between the average In-P and In-CH_2 (ring) distances is 0.441 Å. Since this is somewhat larger than the difference in covalent radii between P and C(sp^3) (i.e., 1.10 - 0.772 Å = 0.33 Å),[17] it appears that the In-P bonds are relatively weak. The In-P distances can be compared to those in $[(Me_3CCH_2)_2InPPh_2]_3$[16] of 2.677 (2) and 2.699 (2) Å. However, since all In-P bonds in $[(Me_3CCH_2)_2InCH_2PPh_2]_2$ can be viewed as donor-acceptor bonds, it might be more appropriate to compare the In-P distance to those in simple adducts such as $Me_3In{\cdot}P(Ph_2)CH_2CH_2(Ph_2)P{\cdot}InMe_3$[18] of 2.755 (4) Å, $Cl_3In{\cdot}2PPh_3$[19] of 2.723 (5) and 2.701 (5) Å, and $Me_3In{\cdot}PMe_3$[18] of 2.683 (4) Å.

The intraring P-C distances are P(1)-C(1′) = P(1′) = C(1) = 1.809 (7) Å [P(2)-C(2′) = P(2′)-C(2) = 1.812 (7)

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[16] Banks, M. A.; Beachley, O. T., Jr.; Buttrey, L. A.; Churchill, M. R.; Fettinger, J. C. *Organometallics* **1991**, *10*, 1901.

[17] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; see Table 7-2, p 224.

[18] Bradley, D C.; Chudzynska, H.; Faktor, M. M.; Frigo, D. M.; Hursthouse, B.; Hussain, B.; Smith, L. *Polyhedron* **1988**, *7*, 1289.

[19] Veidis, M. V.; Palenik, G. J. *J. Chem. Soc. D* **1969**, 586.

Table V. ^{1}H NMR and ^{31}P NMR Spectral Data for $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In) Compounds[a]

	$\delta(PCH_2)$ ($^2J(PCH)$/ $^3J(PMCH)$)	$\delta(CMe_3)$ – $\delta(SiMe_3)$	$\delta(CCH_2)$ – $\delta(SiCH_2)$ ($^3J(PMCH)$)	$^{31}P\{^1H\}$
$[Np_2GaCH_2PPh_2]_2$	1.63 dd (11.7/8.1)	1.03 s	+0.62 d (3.6)	–10.1
$[Np_2InCH_2PPh_2]_2$	1.46 dd (9.9/4.5)	0.90 s	+0.70 d (8.6)	–8.4
$[R_2GaCH_2PPh_2]_2$	1.59 dd (10.8/7.2)	0.11 s	–0.61 d (4.2)	–10.2
$[R_2InCH_2PPh_2]_2$	1.50 dd (10.8/4.5)	0.14 s	–0.57 d (3.6)	–10.0

[a] Np = CH_2CMe_3.

Å], with an average value of 1.811 Å. These are slightly shorter than the predicted P–C(sp^3) single-bond distance of 1.87 Å.

The angles about the indium atoms deviate substantially from the ideal tetrahedral value of 109.47°. The largest angle is that between the two bulky neopentyl ligands, with C(11)–In(1)–C(21) = 122.13 (30)° [C(51)–In(2)–C(61)] = 123.10 (31)°]. The corresponding C–In–C angle in $[(Me_3CCH_2)_2InPPh_2]_3$ is substantially larger at 143.11 (26)°. Intermediate values are found for the CH_2–In–C(neopentyl) angles with C(1)–In(1)–C(11) = 113.57 (27)° and C(1)–In(1)–C(21) = 116.81 (28)° [C(2)–In(2)–C(51) = 113.57 (26)° and C(2)–In(2)–C(61) = 115.69 (30)°]. The smallest angles are the P–In–C angles with P(1)–In(1)–C(1) = 100.76 (19)°, P(1)–In(1)–C(11) = 102.06 (21)°, and P(1)–In(1)–C(21) = 94.85 (22)° [P(2)–In(2)–C(2) = 99.35 (18)°, P(2)–In(2)–C(51) = 101.94 (19)°, and P(2)–In(2)–C(61) = 96.49 (24)°].

Angles about phosphorus also show some irregularities, but to a lesser degree than for indium. Here the most notable feature is that the Ph–P–Ph angles are the smallest, with C(31)–P(1)–C(41) = 101.48 (32)° [C(71)–P(2)–C(81) = 103.08 (32)°]; CH_2–P–Ph angles have intermediate values of 106.92 (33)–108.31 (31)° [106.58 (33)–107.81 (32)°]; In–P–C angles are the largest with values of 108.66 (23)–115.92 (23)° [109.06 (23)–116.86 (35)°].

In–C–C angles involving the α carbons of the neopentyl groups are all expanded from the ideal tetrahedral value, with In(1)–C(11)–C(12) = 120.42 (52)° and In(1)–C(21)–C(22) = 119.35 (57)° [In(2)–C(51)–C(52) = 120.07 (48)° and In(2)–C(61)–C(62) = 122.76 (64)°].

Other distances and angles in the $[(Me_3CCH_2)_2InPPh_2CH_2]_2$ molecules and in the C_6D_6 molecule of solvation (defined by C(91) → C(96)) all lie within the accepted ranges.

The cryoscopic molecular weight studies for benzene solutions suggest the presence of dimers for the compounds in solution as was identified for the solid, $[(Me_3CCH_2)_2InCH_2PPh_2]_2$. The ^{31}P and ^{1}H spectra were also consistent with dimers. The ^{31}P NMR spectral data revealed one concentration-independent resonance at approximately –10 ppm for each compound, $[R_2MCH_2PPh_2]_2$ (M = Ga, In; R = CH_2CMe_3, CH_2SiMe_3) (Table V). Thus, there were no observable changes in the degree of association for any compound on the NMR time scale. The ^{1}H NMR spectral data of the compounds $[R_2MCH_2PPh_2]_2$ (R = CH_2CMe_3, CH_2SiMe_3) consisted of a doublet of doublets that was assigned to the methylene protons of the CH_2PPh_2 substituent, a singlet that was assigned to the CMe_3 of the CH_2YMe_3 (Y = C, Si) substituent, and a doublet that was assigned to the methylene protons of the CH_2YMe_3 (Y = C, Si) substituent. The doublet (CH_2YMe_3) was upfield of the other resonances and appeared even farther upfield when the organic substituent was CH_2SiMe_3 (–0.57 ppm for $[(Me_3SiCH_2)_2InCH_2PPh_2]_2$ and –0.61 ppm for $[(Me_3SiCH_2)_2GaCH_2PPh_2]_2$ as compared to 0.62 and 0.70 ppm for $[(Me_3CCH_2)_2GaCH_2PPh_2]_2$ and $[(Me_3CCH_2)_2InCH_2PPh_2]_2$, respectively). The doublet of doublets appearing in the range 1.46–1.63 ppm was downfield of all the other resonances (except the phenyl protons) and was similar for all the $[R_2MCH_2PPh_2]_2$ compounds.

In conclusion, it is noteworthy that the new compounds $R_2MCH_2PPh_2$ (R = CH_2CMe_3, CH_2SiMe_3; M = Ga, In) are dimers in both the solid and solution phases, especially since these dimeric molecules can be viewed as simple adducts. In contrast, the related adducts $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2$[20] and $(Me_3SiCH_2)_3Ga{\cdot}P(H)Ph_2$[20] are significantly dissociated in benzene solution. The stability of the dimeric molecules $(R_2MCH_2PPh_2)_2$ is further suggested by the observations that the gallium or indium moieties do not form stable room-temperature adducts with Et_2O, THF, TMEDA, or NMe_3. However, the compound $(Me_3SiCH_2)_2GaCH_2PPh_2$ does form an apparent adduct with NMe_3 when a 4-fold excess of NMe_3 is present in benzene solution. The stability of the dimers $(R_2MCH_2PPh_2)_2$ in comparison to the simple adducts might be attributed to an increased Lewis acidity–basicity of the monomers. A more likely reason for the instability of adducts $R_3M{\cdot}P(H)Ph_2$ might be related to the greater solvation enthalpy of the free phosphine by the aromatic solvent benzene. Related solvation effects have been observed previously to be important for explaining the stabilities of other associated group 13–15 compounds.[21]

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: Listings of anisotropic thermal parameters and additional interatomic distances and angles (4 pages); a listing of observed and calculated structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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