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Notes

Synthesis of $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ from $[(Me_3CCH_2)ClGaPPh_2]_3$

O. T. Beachley, Jr.,* and John D. Maloney

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Robin D. Rogers

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

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Summary: The gallium phosphide $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ *has been prepared from* $[(Me_3CCH_2)ClGaPPh_2]_3$ *and* $Li(CMe_3)$ *in an* Et_2O/C_6H_6 *mixture at 0 °C and fully characterized by elemental analyses, physical properties,* ^1H *NMR,* ^{31}P *NMR, and IR spectroscopic data, and an X-ray structural study. The identity of the gallium phosphide was confirmed by its independent synthesis from* $[(Me_3CCH_2)BrGaPPh_2]_3$ *and* $KPPh_2$ *in* Et_2O/C_6H_6*. The dimeric molecule crystallizes in the monoclinic spacegroup* $P\bar{1}$ *with cell dimensions of* $a = 10.106\ (2)$ Å, $b = 11.146\ (6)$ Å, $c = 12.266\ (2)$ Å, $\alpha = 93.91\ (2)°$, $\beta = 101.39\ (1)°$, $\gamma = 95.81\ (4)°$, $V = 1342.0$ Å^3, *and* $Z = 1$*. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer, and the structure was refined to* $R = 3.8\%$ *and* $R_w = 3.8\%$ *for those 3561 unique data with* $F_o \geq 5\sigma(F_o)$*. The four-membered* Ga_2P_2 *ring has a planar conformation. The neopentyl groups are arranged trans to each other across the ring. The bridging Ga–P bond distances are 2.4568 (9) and 2.4689 (9) Å. The terminal Ga–P bond distance is 2.351 (1) Å.*

The synthesis and characterization of heavier group 13 element compounds with three different substituents including two different organic substituents is of interest. The only examples of fully characterized compounds of this type are in indium chemistry and include $[In(CH_2CMe_3)(CH_2SiMe_3)Cl]_2$[1] and $\{In[CH(SiMe_3)_2](i\text{-}Pr)Cl\}_2$.[2] Two other indium compounds of this general type, $[In(CH_2CMe_3)(C_6H_5)Cl]_2$[1] and $[(Me_3CCH_2)(Me_3SiCH_2)InPEt_2]_2$,[1] have been prepared, but neither compound has been characterized by an X-ray structural study. When the syntheses of the closely related gallium compounds[1] $Ga(Me)(CH_2CMe_3)Cl$ and $Ga(CH_2CMe_3)(CH_2CMe_2Ph)Cl$ were attempted, impure products were isolated. The spectroscopic data suggested that ligand redistribution reactions to form symmetrized products had occurred. These observations suggested to us that the chlorine bridges between the gallium atoms in these compounds were apparently too weak to kinetically stabilize a dimer with two different organic substituents. Thus, our goal was to attempt the synthesis of an organogallium compound with two different organic substituents by using a bridging group that would be hopefully stronger than chlorine. The starting material[3] $[(Me_3CCH_2)(Cl)GaPPh_2]_3$ was selected for our synthetic studies. The bridging PPh_2 group was able to stabilize a trimer rather than a dimer, an observation consistent with stronger bridge bonding, but the chloride group would still be available for replacement by a new and different organic group.

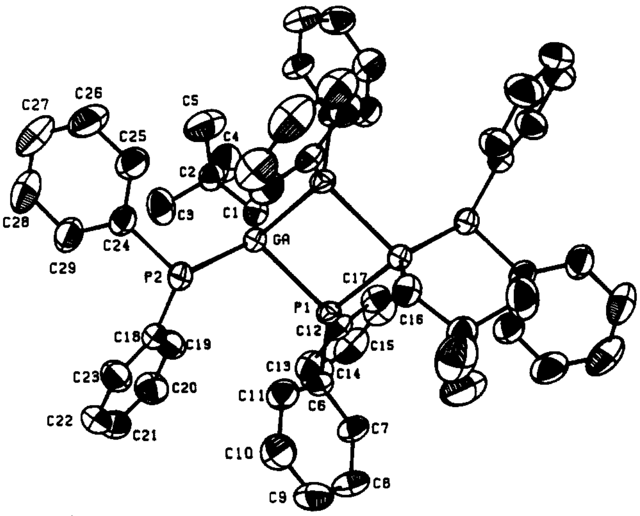

Figure 1. Labeling of atoms in $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ (ORTEP diagram; 50% ellipsoids with hydrogen atoms eliminated for clarity).

The reaction of $[(Me_3CCH_2)ClGaPPh_2]_3$[3] with $LiCMe_3$ in benzene/Et_2O at 0 °C lead to the isolation of $(Me_3CCH_2)Ga(PPh_2)_2$ in 55% yield based upon the monomeric gallium phosphide. This reaction has been repeated, and reproducible results have been obtained. The gallium–phosphorus product was characterized by its physical properties, an X-ray structural study, and ^1H NMR, ^{31}P NMR, and IR spectroscopic data. The identity of the gallium–phosphorus product as $(Me_3CCH_2)Ga(PPh_2)_2$ was also confirmed by its independent synthesis in 80% yield by the reaction of $[(Me_3CCH_2)BrGaPPh_2]_3$[3] with $KPPh_2$ in benzene/Et_2O at 0 °C. The product of this reaction was also fully characterized including C/H analysis. All data suggest that the products from the two reactions are one and the same. The compound had insufficient solubility in benzene for cryoscopic molecular weight determination.

The structure of neopentylgallium bis(diphenylphosphide) consists of dimeric units $[(Me_3CCH_2)Ga(PPh_2)_2]_2$.

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Table I. Interatomic Distances (Å) for $[(Me_3CCH_2)Ga(PPh_2)_2]_2$

(A) Gallium–Phosphorus Distances			
Ga–P(1)	2.4689 (9)	Ga–P(2)	2.351 (1)
Ga–P(1a)[a]	2.4568 (9)		
(B) Gallium–Carbon Distances			
Ga–C(1)	2.001 (3)		
(C) Phosphorus–Carbon Distances			
P(1)–C(6)	1.822 (3)	P(2)–C(18)	1.835 (4)
P(1)–C(12)	1.825 (3)	P(2)–C(24)	1.835 (4)
(D) Neopentyl Carbon–Carbon Distances			
C(1)–C(2)	1.539 (5)	C(2)–C(3)	1.507 (5)
C(2)–C(4)	1.518 (5)	C(2)–C(5)	1.508 (5)
(E) Phenyl Carbon–Carbon Distances			
C(6)–C(7)	1.392 (4)	C(6)–C(11)	1.384 (5)
C(7)–C(8)	1.370 (5)	C(8)–C(9)	1.374 (5)
C(9)–C(10)	1.366 (5)	C(10)–C(11)	1.389 (5)
C(12)–C(13)	1.398 (5)	C(12)–C(17)	1.391 (5)
C(13)–C(14)	1.390 (5)	C(14)–C(15)	1.376 (6)
C(15)–C(16)	1.366 (6)	C(16)–C(17)	1.384 (5)
C(18)–C(19)	1.385 (5)	C(18)–C(23)	1.394 (5)
C(19)–C(20)	1.384 (5)	C(20)–C(21)	1.367 (6)
C(21)–C(22)	1.363 (6)	C(22)–C(23)	1.382 (5)
C(24)–C(25)	1.382 (5)	C(24)–C(29)	1.383 (5)
C(25)–C(26)	1.388 (5)	C(26)–C(27)	1.362 (6)
C(27)–C(28)	1.356 (6)	C(28)–C(29)	1.400 (5)

[a] Atoms designated by "a" are related by the crystallographic center of inversion.

Table II. Angles (deg) for $[(Me_3CCH_2)Ga(PPh_2)_2]_2$

(A) Angles around the Gallium Atom			
P(1)–Ga–P(1a)	84.87 (3)	P(1)–Ga–C(1)	103.4 (1)
P(1)–Ga–P(2)	106.89 (3)	P(2)–Ga–C(1)	131.6 (1)
P(2)–Ga–P(1a)	110.75 (4)	C(1)–Ga–P(1a)	108.7 (1)
(B) Angles around the Phosphorus Atom			
Ga–P(1)–Ga(a)	95.13 (3)	Ga–P(2)–C(18)	104.2 (1)
Ga–P(1)–C(6)	120.8 (1)	Ga–P(2)–C(24)	106.3 (1)
Ga–P(1)–C(12)	108.1 (1)	C(18)–P(2)–C(24)	104.0 (2)
C(6)–P(1)–C(12)	104.2 (2)		
(C) Gallium–Center–Carbon Angles			
Ga–C(1)–C(2)	121.9 (2)		
(D) Phosphorus–Carbon–Carbon Angles			
P(1)–C(6)–C(7)	120.4 (3)	P(1)–C(6)–C(11)	121.5 (3)
P(1)–C(12)–C(13)	119.4 (3)	P(1)–C(12)–C(17)	121.8 (3)
P(2)–C(18)–C(19)	124.9 (3)	P(2)–C(18)–C(23)	117.3 (3)
P(2)–C(24)–C(25)	118.9 (3)	P(2)–C(24)–C(29)	122.9 (3)
(E) Neopentyl Carbon–Carbon–Carbon Angles			
C(1)–C(2)–C(3)	110.7 (3)	C(1)–C(2)–C(4)	110.0 (3)
C(1)–C(2)–C(5)	110.2 (3)	C(3)–C(2)–C(4)	108.8 (4)
C(3)–C(2)–C(5)	109.0 (4)	C(4)–C(2)–C(5)	108.2 (4)
(E) Phenyl Carbon–Carbon–Carbon Angles			
C(7)–C(6)–C(11)	117.9 (3)	C(6)–C(7)–C(8)	121.1 (4)
C(7)–C(8)–C(9)	120.2 (4)	C(8)–C(9)–C(10)	120.0 (4)
C(9)–C(10)–C(11)	120.1 (4)	C(6)–C(11)–C(10)	120.7 (4)
C(13)–C(12)–C(17)	118.7 (3)	C(12)–C(13)–C(14)	119.8 (4)
C(13)–C(14)–C(15)	120.4 (4)	C(14)–C(15)–C(16)	120.2 (4)
C(15)–C(16)–C(17)	120.3 (4)	C(12)–C(17)–C(16)	120.6 (4)
C(19)–C(18)–C(23)	117.8 (4)	C(18)–C(19)–C(20)	120.9 (4)
C(19)–C(20)–C(21)	120.5 (4)	C(20)–C(21)–C(22)	119.4 (4)
C(21)–C(22)–C(23)	121.1 (4)	C(18)–C(23)–C(22)	120.3 (4)
C(25)–C(24)–C(29)	117.9 (4)	C(24)–C(25)–C(26)	121.2 (4)
C(25)–C(26)–C(27)	120.2 (5)	C(26)–C(27)–C(28)	119.8 (4)
C(27)–C(28)–C(29)	120.7 (5)	C(24)–C(29)–C(28)	120.2 (4)

Similar nonbridging groups are arranged trans to each other across the ring. There are no abnormally close contacts in the unit cell. The labeling of the atoms in the molecule is depicted in Figure 1. The interatomic bond distances and angles are listed in Tables I and II.

The four-membered Ga_2P_2 ring of $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ resides around a crystallographic center of inversion and is planar. The related compound[4] $[(Me_3CCH_2)_2GaPPh_2]_2$ has a buckled or butterfly ring geometry whereas $[Bu^n{}_2GaPBu^t{}_2]_2$[5] and $[Bu^t{}_2GaP(H)(C_5H_9)]_2$[6] have planar Ga_2P_2 rings. The bridging Ga–P bond distances in $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ are 2.4568 (9) and 2.4689 (9) Å whereas the terminal Ga–P distances are shorter at 2.351 (1) Å. The bridging Ga–P bond distances are comparable to the distances in $[(Me_3CCH_2)_2GaPPh_2]_2$[4] of 2.479 (3)–2.512 (3) Å and the distances[6] in $[Bu^t{}_2GaP(H)(C_5H_9)]_2$ of 2.451 (1) Å. The shorter terminal Ga–P bond distances of 2.351 (1) Å are comparable to the terminal Ga–P distances of 2.34 (1) Å in the monomeric compound[7] $Ga[P(H)(2,4,6\text{-}Bu^t{}_3C_6H_2)]_3$ and of 2.326 (4) and 2.323 (5) Å in the other monomeric compound[8] $Bu^tGa[P(H)(2,4,6\text{-}Bu^t{}_3C_6H_2]_2$, the distance[9] of 2.338 (1) Å in $[\{(Me_2NCH_2)_2C_6H_3\}GaPSiPh_3]_2$, and the distance of 2.360 Å in gallium phosphide.[10] Thus, it appears unlikely that π bonding is the reason for the terminal gallium–phosphorus distance being shorter than the bridging gallium–phosphorus distance.

Angles within the Ga_2P_2 ring are acute at gallium (P(1)–Ga–P(1a) = 84.87 (3)°) and obtuse at phosphorus (Ga–P–Ga(a) = 95.13 (3)°). The angles within the Ga_2P_2 ring in the closely related molecule[4] $[(Me_3CCH_2)_2GaPPh_2]_2$ are related similarly. The tetrahedral geometry at the gallium(III) atom is irregular. The angle between the terminal and bridging phosphorus atoms at gallium (P(1)–Ga–P(2)) is 106.89 (1)° whereas the terminal phosphorus–gallium–carbon angle (P(2)–Ga–C(1) = 131.6 (1)°) is even larger. The angle between the α-carbon atoms of the terminal neopentyl groups at gallium[4] in $[(Me_3CCH_2)_2GaPPh_2]_2$ are 124.35 (50) and 121.98 (49)°.

The formation of $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ from the reaction of $[(Me_3CCH_2)(Cl)GaPPh_2]_3$ with $LiCMe_3$ demonstrates that dissociation of the initial six-membered ring and rearrangement of the substituents bound to gallium must have occurred. The gallium–phosphorus ring must have come apart for a dimer to be formed from a trimer. Furthermore, ligand redistribution reactions must have occurred for a product with two gallium–phosphorus bonds in the simplest repeating unit to have been formed from a reactant with only one gallium–phosphorus bond in the simplest repeating unit. The diphenylphosphide group is apparently not a sufficiently strong bridging group in these gallium compounds to prevent the breakup of the original six-membered ring. Similarly, the reaction of $[(Me_3CCH_2)(Cl)GaPPh_2]_3$ with $KPPh_2$ to form $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ also confirms that the original six-membered is not maintained during this reaction either. These experimental observations clearly demonstrated that gallium phosphide compounds do not have to maintain their ring structure as they undergo substitution reactions.

The ^1H and ^{31}P NMR spectra of $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ are consistent with the presence of cis and trans

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Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of $[(Me_3CCH_2)Ga(PPh_2)_2]_2$

molecular formula	$C_{58}H_{62}Ga_2P_4$
color/shape	colorless/parallelepiped
mol wt	1022.5
space group	$P\bar{1}$
temp, °C (K)	20 (293)
cell constants[a]	
a, Å	10.106 (2)
b, Å	11.146 (6)
c, Å	12.266 (2)
α, deg	93.91 (4)
β, deg	101.39 (1)
γ, deg	95.81 (4)
V, Å^3	1342.0
Z	1 (dimer)
D_{calcd}, g cm^{-3}	1.27
μ_{calcd}, cm^{-1}	12.19
diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
range of relative transm factors, %	91/100
radiation, graphite monochromator (λ, Å)	Mo Kα (0.710 73)
max cryst dimens, mm	0.30 × 0.33 × 0.40
scan width	0.80 + 0.35 tan θ
std reflcns	300; 050; 007
decay of stds	±2.5%
no. of reflcns measd	4202
2θ range, deg	$2 \leq 2\theta \leq 50$
range of h,k,l	+12,±13,±14
no. of reflcns obsd $[F_o \geq 5\sigma(F_o)]$[b]	3561
computer programs[c]	SHELX[13]
structure solution	SHELXS[14]
no. of params varied	298
weights	$[\sigma(F_o)^2 + 0.0001F_o^2]^{-1}$
GOF	0.47
$R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$	0.038
R_w	0.038
largest feature in final diff map, e Å^{-3}	0.4

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections with $\theta > 19°$. [b] Corrections: Lorentz–polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 15.

isomers of dimeric molecules in d_6-benzene solution. It is regrettable but it is not possible to definitively assign specific lines to a given isomer. However, one might expect on the basis of the solid-state structural study and of steric arguments that the trans isomer might be the more abundant isomer in solution. The ^1H NMR spectrum revealed two singlets at 0.58 and 0.76 ppm for the methyl protons of the neopentyl groups and two multiplets at 1.13 and 1.63 for the methylene protons of the neopentyl groups. The lines at 0.58 and 1.13 ppm are the lines of higher intensity. The multiplets for the methylene protons arise from coupling with the terminal and bridging phosphorus atoms. The $^{31}P\{^1H\}$NMR spectrum consisted of two sets of two triplets each. The triplets of equal intensity at −22.7 and −45.9 ppm are assigned to the terminal and bridging phosphorus atoms, respectively, of the more abundant isomer. These assignments are based on the ^{31}P NMR spectra of $(Me_3CCH_2)_2InPPh_2$,[4] $(Me_3SiCH_2)_2InPPh_2$,[11] and $(Me_3SiCH_2)_2GaPPh_2$,[11] which exist as monomer–dimer equilibrium mixtures. The ^{31}P NMR signal for the monomeric species was downfield of the signal for the dimeric species. Since the monomeric species would have a phosphorus atom analogous to a terminal phosphide in $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ and the phosphorus in the dimeric species is typical of a bridging phosphorus, the downfield signal is assigned to the terminal phosphorus atoms. Triplets arise from phosphorus-31 coupling between the bridging and terminal phosphorus atoms. If the more abundant isomer in solution is the trans isomer, the trans isomer accounts for more than 85% of the species in solution.

Table IV. Final Fractional Coordinates and B(eqv) Values (Å^2) for $[(Me_3CCH_2)Ga(PPh_2)_2]_2$

atom	x/a	y/b	z/c	B(eqv)[a]
Ga	0.09386 (4)	0.07098 (3)	0.13463 (3)	1.96
P(1)	0.02655 (9)	−0.13588 (7)	0.04173 (7)	1.91
P(2)	0.33038 (9)	0.11134 (9)	0.15246 (8)	2.29
C(1)	−0.0245 (4)	0.0809 (3)	0.2470 (3)	2.54
C(2)	0.0015 (4)	0.1843 (3)	0.3412 (3)	2.75
C(3)	0.1381 (4)	0.1827 (5)	0.4170 (3)	4.13
C(4)	−0.1078 (5)	0.1708 (5)	0.4100 (4)	4.92
C(5)	−0.0027 (6)	0.3049 (4)	0.2927 (4)	5.27
C(6)	0.1540 (3)	−0.2301 (3)	0.0108 (3)	2.02
C(7)	0.1226 (4)	−0.3551 (3)	−0.0097 (3)	2.69
C(8)	0.2138 (4)	−0.4263 (3)	−0.0413 (3)	3.46
C(9)	0.3387 (4)	−0.3748 (4)	−0.0536 (4)	3.75
C(10)	0.3726 (4)	−0.2524 (4)	−0.0335 (4)	3.67
C(11)	0.2803 (4)	−0.1797 (4)	−0.0022 (3)	2.94
C(12)	−0.0635 (4)	−0.2241 (3)	0.1303 (3)	2.19
C(13)	0.0104 (4)	−0.2833 (3)	0.2148 (3)	2.96
C(14)	−0.0571 (5)	−0.3483 (4)	0.2844 (3)	3.93
C(15)	−0.1958 (5)	−0.3529 (4)	0.2719 (4)	4.27
C(16)	−0.2687 (5)	−0.2939 (4)	0.1907 (4)	3.89
C(17)	−0.2036 (4)	−0.2294 (3)	0.1199 (3)	2.87
C(18)	0.4006 (4)	0.0093 (3)	0.2544 (3)	2.37
C(19)	0.3269 (4)	−0.0559 (4)	0.3193 (3)	3.19
C(20)	0.3875 (5)	−0.1340 (4)	0.3914 (4)	3.89
C(21)	0.5223 (5)	−0.1470 (4)	0.4014 (4)	3.77
C(22)	0.5964 (4)	−0.0835 (4)	0.3383 (4)	3.74
C(23)	0.5372 (4)	−0.0070 (4)	0.2639 (4)	3.27
C(24)	0.3796 (4)	0.2628 (3)	0.2268 (3)	2.48
C(25)	0.3238 (4)	0.3601 (4)	0.1798 (4)	3.49
C(26)	0.3647 (5)	0.4775 (4)	0.2285 (4)	4.40
C(27)	0.4631 (6)	0.4989 (4)	0.3232 (4)	4.65
C(28)	0.5206 (5)	0.4051 (4)	0.3704 (4)	4.39
C(29)	0.4804 (4)	0.2861 (4)	0.3224 (3)	3.43

[a] $B(\mathrm{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

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. Solvents were dried by conventional procedures. The compounds[3] $(Me_3CCH_2)ClGaPPh_2$ and $(Me_3CCH_2)BrGaPPh_2$ were prepared and purified by literature methods. *tert*-butyllithium was purchased as a 1.7 M solution in pentane from Aldrich. The pentane was removed by vacuum distillation, and $LiCMe_3$ was purified by sublimation at 50 °C. Diphenylphosphine was purchased from Strem Chemicals, Inc., and was purified by distillation. Potassium diphenylphosphide[12] ($KPPh_2$) was prepared from excess diphenylphosphine and KH in diethyl ether. 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. The ^1H NMR spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 ppm and C_6D_6 at δ 7.15 ppm. The ^{31}P NMR spectrum was recorded at 161.9 MHz on a Varian VXR-400 spectrometer. Proton-decoupled ^{31}P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries and are uncorrected.

Reaction of $(Me_3CCH_2)ClGaPPh_2$ with $LiCMe_3$. A side-arm dumper charged with 0.221 g (3.45 mmol) of $LiCMe_3$ was

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attached to a two-neck flask which contained 1.249 g (3.455 mmol) of $(Me_3CCH_2)ClGaPPh_2$ dissolved in a mixture of 10 mL of benzene and 20 mL of Et_2O. After the mixture was cooled to 0 °C, the $LiCMe_3$ was added slowly. The resulting mixture was stirred for 18 h at ambient temperature, and then the solvents were removed by vacuum distillation. The two-neck flask was fitted with a medium frit equipped with a Schlenk receiving vessel. Three extractions with 30 mL of benzene provided a soluble brown goo. The brown goo was then washed twice with 15 mL of anhydrous pentane to leave a pentane-insoluble, colorless solid (0.438 g, 0.946 mmol, 54.8% yield of $(Me_3CCH_2)Ga(PPh_2)_2$). Recrystallization of $(Me_3CCH_2)Ga(PPh_2)_2$ by using slow diffusion of anhydrous pentane into a saturated benzene solution afforded crystallographic quality crystals.

$(Me_3CCH_2)Ga(PPh_2)_2$. Mp: 206–210 °C dec. ^{1}H NMR (C_6D_6, δ): 0.58 (s, 8.8 H, $-CMe_3$), 0.76 (s, 1.1 H, $-CMe_3$), 1.13 (m, 2.0 H, $-CH_2-$), 1.63 (m, 0.3 H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −22.7 (t, $^2J_{PGaP}$ = 27.5 Hz, 9.0), −25.0 (t, $^2J_{PGaP}$ = 35.2 Hz, 1.2), −45.9 (t, $^2J_{PGaP}$ = 29.1 Hz, 8.2), −49.4 (t, $^2J_{PGaP}$ = 34.0 Hz, 1.0). IR (Nujol mull cm^{-1}): 1582 (m), 1569 (w), 1479 (m), 1432 (m), 1377 (m), 1365 (m), 1359 (m), 1236 (vw), 1159 (vw), 1134 (w), 1104 (vw), 1093 (vw), 1070 (vw), 1026 (m), 1002 (vw), 747 (sh), 742 (vs), 736 (m), 721 (w), 709 (m), 700 (s), 690 (w), 595 (w), 504 (m), 479 (m).

Synthesis of $(Me_3CCH_2)Ga(PPh_2)_2$. To a solution of $(Me_3CCH_2)BrGaPPh_2$ (0.945 g, 2.33 mmol) in a mixture of 20 mL of benzene and 10 mL of Et_2O at 0 °C was added $KPPh_2$ (0.522 g, 2.33 mmol). The resulting mixture was stirred for 20 h at ambient temperature. Repetitive extractions with benzene provided a crude product which was washed with 15 mL of anhydrous pentane at ambient temperature to yield 0.867 g of $(Me_3CCH_2)Ga(PPh_2)_2$ (1.87 mmol, 80.4% based on $(Me_3CCH_2)BrGaPPh_2$). The product was recrystallized from a standard benzene solution layered with pentane.

$(Me_3CCH_2)Ga(PPh_2)_2$. Mp: 218–219 °C dec. ^{1}H NMR (C_6D_6, δ): 0.60 (s, 9.1 H, $-CMe_3$), 0.78 (s, 0.9 H, $-CMe_3$), 1.15 (m, 2.0 H, $-CH_2-$), 1.63 (m, 0.2 H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): −22.4 (t, $^2J_{PGaP}$ = 28.7 Hz, 10.4), −24.3 (t, $^2J_{PGAP}$ = 32.9 Hz, 1.0), −45.6 (t, $^2J_{PGaP}$ = 28.3 Hz, 7.7), −48.7 (t, $^2J_{PGaP}$ = 33.8 Hz, 1.1). Anal. Calcd: C, 68.13; H, 6.11. Found: C, 68.18; H, 6.09. IR (Nujol mull cm^{-1}): 1579 (m), 1565 (w), 1475 (m), 1428 (m), 1373 (m), 1360 (m), 1355 (m), 1232 (vw), 1155 (w), 1130 (w), 1099 (vw), 1088 (vw), 1067 (vw), 1022 (m), 998 (vw), 745 (sh), 738 (vs), 732 (s), 719 (w), 705 (m), 695 (sh), 690 (s), 592 (w), 500 (m), 475 (m).

X-ray Data Collection, Structure Determination, and Refinement for $[(Me_3CCH_2)Ga(PPh_2)_2]_2$. A transparent crystal of the title compound was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table III.

Least-squares refinement with isotropic thermal parameters led to $R = 0.075$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.038$ and $R_w = 0.038$. The final values of the positional parameters are given in Table IV.

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Supplementary Material Available: Listings of anisotropic thermal parameters, calculated positions of hydrogen atoms, and least-squares planes for $[(Me_3CCH_2)Ga(PPh_2)_2]_2$ (4 pages). Ordering information is given on any current masthead page.

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