Organometallics **1997,** *16,* 3267−3272

Cyclopentadiene Elimination Reaction as a Route to Bis(neopentyl)gallium Phosphides. Crystal and Molecular Structures of $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$

O. T. Beachley, Jr.,*,† John P. Maloney,† and Robin D. Rogers‡

Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260, and The University of Alabama, Tuscaloosa, Alabama 35487

Received February 6, 1997⊗

The compound $(Me_3CCH_2)_2Ga(C_5H_5)$ has been observed to react at room temperature in pentane solution with $HPEt_2$ and $H_2P(C_6H_{11})$ to eliminate C_5H_6 and form $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaP(H)(C_6H_{11})]_2$, respectively. The additional new compound $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$ was prepared by a metathetical reaction between $Ga(CH_2CMe_3)_2Cl$ and $LiP(C_6H_{11})_2$ in diethyl ether. All three compounds were fully characterized in solution, whereas two of the three, $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$, were characterized by X-ray structural studies.

A major challenge for synthetic group 13 chemistry is to discover new reactions for the preparation of ultrapure precursors for electronic materials. Thus, the simplest and most direct route which involves the most limited number of synthetic steps from the fewest reagents of high purity at the lowest possible reaction temperature should minimize the introduction of impurities. Consequently, our research has been directed toward the use of the hydrocarbon elimination reaction[1] and the search for novel examples which occur at or below room temperature. The cyclopentadiene elimination reaction (eq 1) between $R_2Ga(C_5H_5)$ (R = Me,[2] Et[3]) and either amines, phosphines, or thiols is an example of an elimination reaction which typically occurs at or below room temperature. Our studies of these reactions[2,3] suggested that the association of the initial group 13−15 monomeric product and/or removal of the cyclopentadiene monomer by either dimerization or distillation was necessary to minimize the occurrence of the back-reaction for eq 1 and produce high yields of the desired product. The study of the cyclopentadiene elimination reaction is made more interesting with the realization that even though $R_2Ga(C_5H_5)$ (R = Me,[4] Et[5]) can be prepared by a stoichiometric ligand redistribution reaction from GaR_3 and $Ga(C_5H_5)_3$, isolated by sublimation, and fully characterized by elemental analyses and X-ray structural studies, neither compound exists in solution as a single compound. Both compounds undergo ligand restribution reactions upon dissolution in benzene to form equilibrium mixtures of $R_2Ga(C_5H_5)$, $RGa(C_5H_5)_2$ and GaR_3 (eq 2). Thus, research projects

$$R_2Ga(C_5H_5) + HER'_2 \rightarrow {}^1/_2[R_2GaER'_2]_2 + C_5H_6 \quad (1)$$

$$2R_2Ga(C_5H_5) \rightleftharpoons RGa(C_5H_5)_2 + GaR_3 \quad (2)$$

have been designed to attempt to learn more about the reactivity patterns of the multiple gallium species which are present in a solution and about the effects of the organic substituents on gallium on the usefulness of the cyclopentadiene elimination reaction for the preparation of single-source precursors.

The cyclopentadienide group has been shown to be a facile deprotonating group for phosphines when the organogallium reagent was either $Me_2Ga(C_5H_5)$[2] or $Et_2Ga(C_5H_5)$.[3] In order to test whether the cyclopentadienide ligand could be incorporated into a gallium compound which had two bulky organic substituents, $(Me_3CCH_2)_2Ga(C_5H_5)$ was prepared *in situ* and used to study elimination reactions. The phosphide derivative $[(Me_3CCH_2)_2GaPEt_2]_2$ was prepared readily at room temperature by combining $Ga(CH_2CMe_3)_3$,[6] $Ga(C_5H_5)_3$,[7] and $HPEt_2$ in a 2:1:3 mol ratio, respectively, in pentane (eq 3). After the phosphine was added to the solution

$$2Ga(CH_2CMe_3)_3 + Ga(C_5H_5)_3 + 3HPEt_2 \rightarrow 3(Me_3CCH_2)_2GaPEt_2 + 3C_5H_6 \quad (3)$$

formed from the two gallium compounds, the resulting solution was stirred for 18 h. All volatile components were then removed by vacuum distillation. The product was washed first with pentane at low temperature (−78 °C) and then purified by recrystallization to produce $(Me_3CCH_2)_2GaPEt_2$ as a colorless crystalline solid in 45% yield. Even though the yield of $(Me_3CCH_2)_2GaPEt_2$ was only 45%, there was no evidence to suggest the formation of any other gallium−phosphorus product. No data suggested the elimination of neopentane with formation of the unsymmetrically-substituted product $(Me_3CCH_2)(C_5H_5)GaPEt_2$. Thus, the very high solubility

---

† State University of New York at Buffalo.

‡ The University of Alabama.

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) Beachley, O. T., Jr.; Coates, G. E. J. *Chem. Soc.* **1965**, 3241.

(2) Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1976.

(3) Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Toomey, L. M. *Organometallics* **1996**, *15*, 3653.

(4) Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R. *J. Organomet. Chem.* **1992**, *434*, 11.

(5) Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Krajkowski, L. M. *Organometallics* **1995**, *14*, 4402.

(6) Beachley, O. T., Jr.; Pazik, J. P. *Organometallics* **1988**, *7*, 1516.

(7) Beachley, O. T., Jr.; Getman, T. D.; Kirss, R. U.; Hallock,R. B.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 751.

S0276-7333(97)00090-3 CCC: $14.00

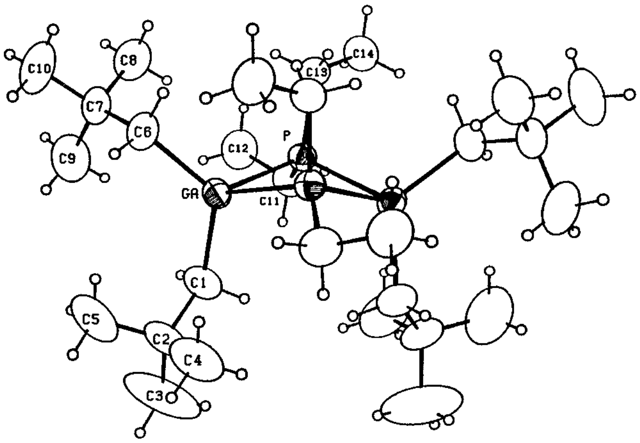

Figure 1. Molecular geometry of $[(Me_3CCH_2)_2GaPEt_2]_2$. ORTEP diagram for non-hydrogen atoms, with hydrogen atoms arbitrarily reduced in size for clarity.

Table 1. Important Interatomic Distances[a] (Å) and Angles (deg) for $[(Me_3CCH_2)_2GaPEt_2]_2$

	Bond Distances (Å)		
Ga−P	2.450(1)	Ga−P(a)	2.452(1)
Ga−C(1)	1.998(5)	Ga−C(6)	2.006(4)
P−C(11)	1.844(4)	P−C(13)	1.847(4)
	Bond Angles (deg)		
P−Ga−C(1)	100.5(1)	P−Ga−C(6)	120.8(1)
C(1)−Ga−C(6)	124.1(2)	P−Ga−P(a)	80.47(5)
C(1)−Ga−P(a)	114.4(1)	C(6)−Ga−P(a)	108.6(1)
Ga−P−Ga(a)	93.43(6)	C(11)−P−Ga(a)	122.5(1)
C(13)−P−Ga(a)	107.6(1)	Ga−P−C(11)	114.4(2)
Ga−P−C(13)	115.7(1)	C(11)−P−C(13)	103.7(2)
Ga−C(1)−C(2)	122.9(3)	Ga−C(6)−C(7)	122.8(3)
P−C(11)−C(12)	114.7(3)	P−C(13)−C(14)	115.6(3)

[a] Symmetry code = 2 − *x*, *y*, $^3/_2$ − *z*.

of $(Me_3CCH_2)_2GaPEt_2$ in pentane, even at low temperature (−78 °C), was probably responsible for the observed low yield. Bis(neopentyl)gallium diethylphosphide was fully characterized by elemental analyses for C and H, melting point, cryoscopic molecular weight studies, infrared, ^1H and ^{31}P NMR spectroscopy, and an X-ray structural study. All data are consistent with the presence of only dimers $[(Me_3CCH_2)_2GaPEt_2]_2$ in all phases studied. The facile elimination of cyclopentadiene between $(Me_3CCH_2)_2Ga(C_5H_5)$ and $HPEt_2$ should be compared with the observation that $Ga(CH_2CMe_3)_3$ and $HPEt_2$ did not react to eliminate CMe_4, even when a benzene solution was heated at 70 °C for 3 weeks.

Dimeric units with the formula $[(Me_3CCH_2)_2GaPEt_2]_2$ were identified by the X-ray structural study of the crystalline product isolated from the reaction of $(Me_3CCH_2)_2Ga(C_5H_5)$ with $HPEt_2$. The solid state structure and labeling of the atoms in the molecule are shown in Figure 1. Interatomic bond distances and angles are listed in Tables 1. There were no abnormally close contacts in the unit cell. The most noteworthy feature about the structure is the buckled or butterfly-shaped Ga_2P_2 ring. The only other symmetrically-substituted gallium phosphorus compound with this type of structure is $[(Me_3CCH_2)_2GaPPh_2]_2$.[8] The dihedral or fold angles for $[(Me_3CCH_2)_2GaPEt_2]_2$, 153.9° about gallium and 154.0° about phosphorus, are larger and closer to planar than the corresponding dihedral angles for $[(Me_3CCH_2)_2GaPPh_2]_2$, 142.2° and 145.6°. The folding of the four-membered ring has been suggested to result from a variety of possible factors including steric interactions between the neopentyl groups and/or the phosphorus substituents and intermolecular interactions within the unit cell.[8] Each gallium and each phosphorus atom has a distorted tetrahedral coordination environment. The smallest angles in the molecule are those between the atoms in the ring. The P−Ga−P(a) angle is 80.47 (5)° and Ga−P−Ga(a) is 93.43 (6)°. The angle between the two α-carbon atoms of the neopentyl groups bonded to gallium C(1)−Ga−C(6) is 124.1(2)°. In constast, the angle between the two α-carbon atoms of the ethyl groups on phosphorus C(11)−P−C(13) is 103.7(2)°. The Ga−P bond distances, 2.450(1) and 2.452(1) Å, are comparable to the corresponding distances of 2.479(3), 2.482 (3), 2.488 (3), and 2.512(3) Å observed for $[(Me_3CCH_2)_2GaPPh_2]_2$.[8] All other distances and angles in $[(Me_3CCH_2)_2GaPEt_2]_2$ appear normal.

Cryoscopic molecular weight and NMR spectral studies indicate that $(Me_3CCH_2)_2GaPEt_2$ exists as a dimer in benzene solution. The combination of the absence of a concentration dependence for the observed molecular weight and the presence of only one line in the ^{31}P NMR spectrum at −50.1 ppm is consistent with the presence of only one species in solution. The chemical shifts and multiplicities of the lines which arise from the coupling of proton(s) to the two phosphorus atoms in the ^1H NMR spectrum also support the presence of a dimer. Furthermore, the spectrum of $[(Me_3CCH_2)_2GaPEt_2]_2$ was very similar to that observed for $[(Me_3CCH_2)_2InPEt_2]_2$.[9]

The compound $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$ was also prepared readily by a room temperature cyclopentadiene elimination reaction by combining $Ga(CH_2CMe_3)_3$,[6] $Ga(C_5H_5)_3$,[7] and $H_2P(C_6H_{11})$ in a 2:1:3 mol ratio, respectively, in pentane (eq 4). There were no data to suggest

$$2Ga(CH_2CMe_3)_3 + Ga(C_5H_5)_3 + 3HP(H)(C_6H_{11}) \rightarrow 3(Me_3CCH_2)_2GaP(H)(C_6H_{11}) + 3C_5H_6 \quad (4)$$

the formation of either neopentane or $(Me_3CCH_2)(C_5H_5)GaP(H)(C_6H_{11})$ from these reagents. The gallium phosphide product was isolated in approximately 70% yield and was characterized by C and H elemental analyses, melting point, and IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopies. Additional characterization by cryoscopic molecular weight studies and X-ray structural studies were unsuccessful. Even though cooling of the dilute benzene solutions for cryoscopic molecular weight studies lead to crystallization of the compound, crystals suitable for an X-ray structural study could not be obtained.

Extensive ^{31}P, ^{13}C, and ^1H NMR spectral studies suggest that $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$ exists in benzene and toluene solutions as a dimer with the bulky cyclohexyl groups oriented trans to each other in order to minimize the steric effects between the cyclohexyl groups. A more detailed examination of a model of this molecule reveals that two different orientations of the cyclohexyl group are possible if rotation of the cyclohexyl group is restricted. These orientations are distinguished by the relationships between the hydrogen bonded to the α-carbon atom of the cyclohexyl group and the hydrogen bonded to phosphorus. These protons can

---

(8) Banks, M. A.; Beachley, O. T., Jr.; Buttrey, L. A.; Churchill, M. R.; Fettinger, J. C. *Organometallics* **1991**, *10*, 1901.

(9) Beachley, O. T., Jr.; Maloney, J. D.; Banks, M. A.; Rogers, R. D. *Organometallics* **1995**, *14*, 3448.

be on the same side or on opposite sides and, thus, be *syn* and *anti* to each other. The cyclohexyl group is bonded to phosphorus, most likely through its equatorial position as was observed for $[(Me_3CCH_2)_2InP(H)(C_6H_{11})]_3$[9] and $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$. Thus, a given dimer can have two pairs of *syn* protons, two pairs of *anti* protons, or one pair of *syn* and one pair of *anti* protons. These *syn* and *anti* protons are magnetically nonequivalent and, in turn, make the phosphorus atoms and the atoms in the cyclohexyl and neopentyl groups in the molecule distinguishable by NMR spectroscopy. Thus, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 has two concentration-independent lines at −63.60 and −73.26 ppm (peak heights of 17.5 and 20.6 units and with widths-at-half-height of approximately eight and six units, respectively). When phosphorus was coupled to the proton, each line was a doublet of doublets. Thus, one line is due to a phosphorus with *syn* protons, whereas the other is for the phosphorus with *anti* protons. It is not possible to assign a given line to a specific conformation or molecular structure. An alternate interpretation of the ^{31}P NMR spectrum would assign these resonances to cis and to trans geometrical isomers. However, other NMR spectra do not support this hypothesis. Similarly, an equilibrium between species of two different degrees of association, such as monomer−dimer or dimer−trimer, is also inconsistent with the data because the spectrum was concentration independent. A variable-temperature NMR experiment was used in an attempt to confirm the hypothesis of *syn* and *anti* protons. However, the ^{31}P NMR spectrum at 100 °C, the highest temperature used for the toluene solution, had only two lines −64.1 and −73.3 ppm and was not significantly different from the room temperature spectrum. Thus, since neither the chemical shifts nor the intensities changed significantly, 100 °C does not supply sufficient energy to allow for free rotation of the $P-C(C_6H_{11})$ bonds in this molecule. The $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 has two sets of closely spaced lines and provides support for the hypothesis of a trans isomer(s) with *syn* and *anti* protons. The lines at 25.4 and 27.1 ppm of approximately equal intensity are assigned to magnetically nonequivalent methylene carbon atoms in neopentyl groups; the lines at 34.1 and 34.3 ppm are assigned to the two different types of tertiary carbon atoms of the neopentyl groups; the lines at 36.0 and 36.2 ppm are assigned to the magnetically different types of *tert*-butyl carbon atoms for the neopentyl groups; whereas the eight lines between 31.0 and 32.7 ppm are assigned to the carbon atoms of two magnetically nonequivalent cyclohexyl groups. If cis and trans geometrical isomers were present in almost equal concentrations, three sets of $^{13}C\{^1H\}$ lines would be expected, one set for the trans isomer and two sets for the cis isomer. The ^1H NMR spectrum had extensive overlapping of lines for the neopentyl and cyclohexyl groups and, thus, was essentially uninformative. However, two doublets of doublets at 2.99 and 3.43 ppm for the hydrogen atoms bonded to phosphorus were clearly discernable.

Even though the simple neopentane elimination reaction between $Ga(CH_2CMe_3)_3$ and $HP(C_6H_{11})_2$ in a benzene solution at 70 °C cannot be used to prepare $(Me_3CCH_2)_2GaP(C_6H_{11})_2$, the compound was synthesized in higher than 80% yield by a metathetical reaction between $Ga(CH_2CMe_3)_2Cl$[6] and $LiP(C_6H_{11})_2$ in diethyl ether at 0 °C. The compound $(Me_3CCH_2)_2GaP(C_6H_{11})_2$ was fully characterized by C and H elemental analyses, melting point, cryoscopic molecular weight studies, IR and ^1H and ^{31}P NMR spectroscopies, and an X-ray structural study. All data are consistent with the conclusion that dimers exist in all phases studied. The cyclopentadiene elimination reaction was not investigated as a potential route to $(Me_3CCH_2)_2GaP(C_6H_{11})_2$.

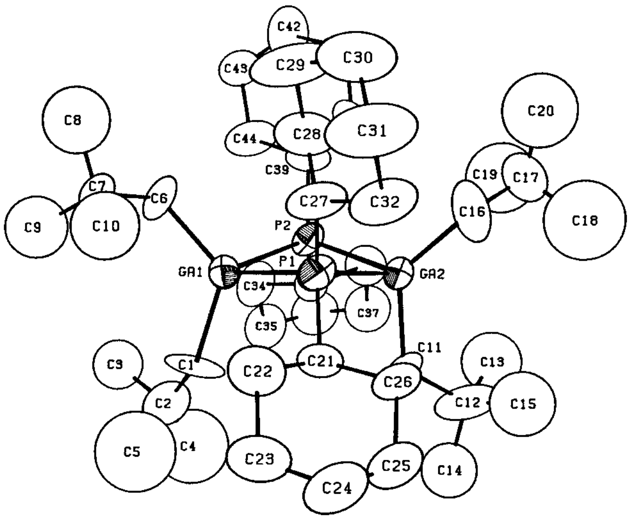

Figure 2. Molecular geometry of $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$ (molecule A). ORTEP diagram for non-hydrogen atoms.

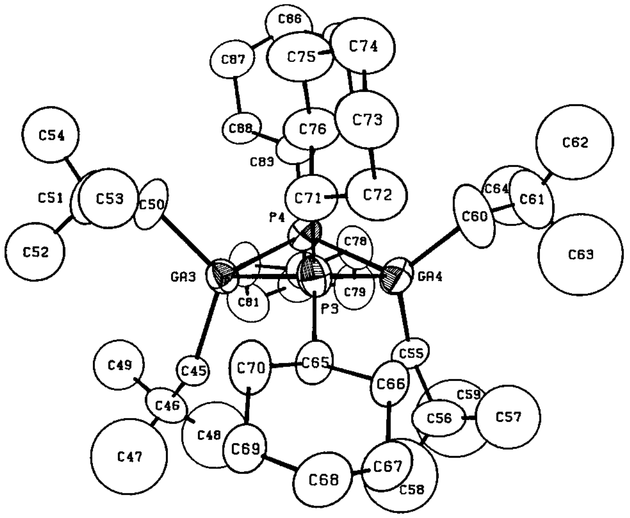

Figure 3. Molecular geometry of $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$ (molecule B). ORTEP diagram for non-hydrogen atoms, with hydrogen atoms omitted for clarity.

Crystals of bis(neopentyl)gallium bis(cyclohexyl)phosphide consisted of discrete dimeric units with the formula $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$. The unit cell contained two very similar but different molecules (molecule A, Figure 2, and molecule B, Figure 3). Interatomic bond distances and angles for each of these molecules are collected in Table 2. There were no abnormally close contacts in the unit cell. This structural determination suffered from high thermal motion and disorder, which is consistent with the large sterically bulky nature of the molecule. All 24 of the methyl groups for the two unique molecules in the asymmetric unit appear to be freely rotating or have multiple orientations. It was not possible to resolve disordered positions for these atoms. Thus, each methyl carbon was refined with isotopic thermal parameters which

Table 2. Important Interatomic Distances (Å) and Angles (deg) for $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$

Bond Distances (Å)-Molecule A			
Ga(1)−P(1)	2.463(3)	Ga(1)−P(2)	2.476(3)
Ga(1)−C(1)	2.02(3)	Ga(1)−C(1)′	2.07(3)
Ga(1)−C(6)	2.006(9)	Ga(2)−P(1)	2.463(3)
Ga(2)−P(2)	2.460(3)	Ga(2)−C(11)	2.02(1)
Ga(2)−C(16)	2.02(2)	P(1)−C(21)	1.88(1)
P(1)−C(27)	1.88(1)	P(2)−C(33)	1.89(1)
P(2)−C(39)	1.85(1)		
Bond Distances (Å)-Molecule B			
Ga(3)−P(3)	2.465(3)	Ga(3)−P(4)	2.463(3)
Ga(3)−C(45)	2.01(2)	Ga(3)−C(45)′	2.08(3)
Ga(3)−C(50)	2.07(1)	Ga(4)−P(3)	2.481(3)
Ga(4)−P(4)	2.481(3)	Ga(4)−C(55)	2.09(2)
Ga(4)−C(55)′	2.12(2)	Ga(4)−C(60)	2.01(2)
P(3)−C(65)	1.87(1)	P(3)−C(71)	1.89(1)
P(4)−C(77)	1.89(1)	P(4)−C(83)	1.86(1)
Bond Angles (deg)-Molecule A			
P(1)−Ga(1)−P(2)	84.3(1)	P(1)−Ga(1)−C(1)	99.6(9)
P(2)−Ga(1)−C(1)	121.6(8)	P(1)−Ga(1)−C(1)′	101.9(9)
P(2)−Ga(1)−C(1)′	91(1)	P(1)−Ga(1)−C(6)	117.2(4)
P(2)−Ga(1)−C(6)	106.4(4)	C(1)−Ga(1)−C(6)	121.8(8)
C(1)′−Ga(1)−C(6)	138(1)	P(1)−Ga(2)−P(2)	84.6(1)
P(1)−Ga(2)−C(11)	101.8(3)	P(2)−Ga(2)−C(11)	102.9(4)
P(1)−Ga(2)−C(16)	101.4(6)	P(2)−Ga(2)−C(16)	123.6(5)
C(11)−Ga(2)−C(16)	129.3(6)	Ga(1)−P(1)−Ga(2)	93.1(1)
Ga(1)−P(1)−C(21)	110.1(4)	Ga(2)−P(1)−C(21)	109.2(3)
Ga(1)−P(1)−C(27)	116.7(4)	Ga(2)−P(1)−C(27)	121.6(5)
C(21)−P(1)−C(27)	105.7(6)	Ga(1)−P(2)−Ga(2)	92.8(1)
Ga(1)−P(2)−C(33)	115.8(4)	Ga(2)−P(2)−C(33)	108.0(3)
Ga(1)−P(2)−C(39)	116.0(4)	Ga(2)−P(2)−C(39)	115.4(5)
C(33)−P(2)−C(39)	108.1(6)	Ga(1)−C(1)−C(2)	131(2)
Ga(1)−C(1)′−C(2)	119(2)	Ga(1)−C(6)−C(7)	124.1(9)
Ga(2)−C(11)−C(12)	124(1)	Ga(2)−C(16)−C(17)	133(2)
P(1)−C(27)−C(28)	109(1)	P(1)−C(27)−C(32)	114.0(8)
P(1)−C(21)−C(22)	112.1(7)	P(1)−C(21)−C(26)	113.8(9)
P(2)−C(39)−C(40)	126(1)	P(2)−C(39)−C(44)	115(1)
P(2)−C(39)−C(40)′	113(1)		
Bond Angles (deg)-Molecule B			
P(3)−Ga(3)−P(4)	84.3(1)	P(3)−Ga(3)−C(45)	100.3(6)
P(4)−Ga(3)−C(45)	126.4(5)	P(3)−Ga(3)−−C(45)′	97.8(8)
P(4)−Ga(3)−C(45)′	92.8(8)	P(3)−Ga(3)−C(50)	119.9(4)
P(4)−Ga(3)−C(50)	104.1(4)	C(45)−Ga(3)−C(50)	118.0(6)
C(45)′−Ga(3)−C(50)	139.6(8)	P(3)−Ga(4)−P(4)	83.6(1)
P(3)−Ga(4)−C(55)	123.6(7)	P(4)−Ga(4)−C(55)	95.5(7)
P(3)−Ga(4)−C(55)′	91.2(6)	P(4)−Ga(4)−C(55)′	96.8(7)
P(3)−Ga(4)−C(60)	106.5(4)	P(4)−Ga(4)−C(60)	120.8(5)
C(55)−Ga(4)−C(60)	121.0(8)	C(55)′−Ga(4)−C(60)	139.5(8)
Ga(3)−P(3)−Ga(4)	91.8(1)	Ga(3)−P(3)−C(65)	109.5(4)
Ga(4)−P(3)−C(65)	112.5(3)	Ga(3)−P(3)−C(71)	113.5(4)
Ga(4)−P(3)−C(71)	119.6(5)	C(65)−P(3)−C(71)	108.7(6)
Ga(3)−P(4)−Ga(4)	91.9(1)	Ga(3)−P(4)−C(77)	114.5(4)
Ga(4)−P(4)−C(77)	111.2(3)	Ga(3)−P(4)−C(83)	108.8(4)
Ga(4)−P(4)−C(83)	117.6(4)	C(77)−P(4)−C(83)	111.6(6)
Ga(3)−C(45)−C(46)	126(1)	Ga(3)−C(45)′−C(46)	112(1)
Ga(3)−C(50)−C(51)	124(1)	Ga(4)−C(60)−C(61)	127(1)
Ga(4)−C(55)−C(56)	124(2)	Ga(4)−C(55)−C(59)	158(2)
		Ga(4)−C(55)′−C(56)	117(1)
P(3)−C(71)−C(72)	114.0(8)	P(3)−C(71)−C(76)	108.3(8)
P(4)−C(77)−C(78)	111.8(8)	P(4)−C(77)−C(82)	113.8(6)
P(4)−C(83)−C(84)	115.5(7)	P(4)−C(83)−C(88)	115.8(9)

proved to be quite large. However, it was possible to refine two alternate positions of 50% occupancy each for three of the eight unique methylene carbon atoms bonded to gallium. C(1), C(45), and C(55) were refined in two orientations with the alternate orientation designated with a prime (C(1)′, C(45)′, and C(55)′). Although several of the other carbon atoms bonded to gallium may also have been fractionally disordered, as evidenced by elongated anisotropic thermal ellipsoids, it was not possible to resolve the different positions.

The most interesting part of the disorder model involves the cyclohexyl groups. In molecule A (Ga(1), Ga(2)), one cyclohexyl group bonded to P(2) is disordered. The carbon bonded to phosphorus (C(39)) and one of the adjacent ring carbon atoms (C(44)) are ordered and common to both orientations. The remaining four carbon atoms (C(40)−C(43)) are disordered and were resolved into two orientations at 50% occupancy each.

The cyclohexyl ring disorder in molecule A produces two orientations, one of which is identical to the conformation found in molecule B (Ga(3), Ga(4)) and one of which is different. In molecule B and molecule A containing C(40)−C(43), three of the cyclohexyl groups (C(21), C(33), C(39); C(65), C(77), C(83)) are arranged in a propeller-like fashion around the Ga_2P_2 ring. The fourth cyclohexyl group in each molecule (C(27); C(71)) is twisted 90° relative to the other three. The uniquely oriented cyclohexyl groups (C(27); C(71)) are bonded to P(1) in molecule A and P(3) in molecule B and are located such that the gallium atoms in the Ga_2P_2 ring bend away from these groups.

The disordered positions of the cyclohexyl goup in molecule A (C(40)′−C(43)′) produce a different orientation. The disordered cyclohexyl group in molecule A (C(39)) is on the same side of the Ga_2P_2 ring as the cyclohexyl group above which is twisted 90° relative to the other three (C(27)). The effect of the disorder is such that this cyclohexyl group is also twisted 90° relative to the propeller-like orientations (C(21), C(33)). Thus, in one conformation of molecule A, both cyclohexyl groups, located in such a way that the gallium atoms in the Ga_2P_2 ring bend away from them, are twisted 90° relative to the remaining two rings.

The presence of two unique molecules in the asymmetric unit may be the result of the differences in conformation found for the disordered models. Although disorder and high thermal motion reduce the quality of the structural results, the general features of the Ga_2P_2 ring and the orientations of the ligands about the ring are quite evident. It is clear that the four-membered Ga_2P_2 ring has a folded or butterfly-shaped ring similar to that observed for $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaPPh_2]_2$.[8] The dihedral or fold angles for the four-membered rings for molecule A and B are different, 154.6° about gallium and 156.4° about phosphorus for molecule A (Table 2) and 148.2° and 150.3°, respectively, for molecule B. This observation might suggest that crystal packing forces are more important than the steric effects of the ligands in the molecule as a cause for the folding of the four-membered ring. The constraints of the four-membered ring which reduce the internal ring angles from the normal tetrahedral value in turn increase the angles between the α-carbon atoms of the neopentyl groups bound to gallium. Similar observations have been made for the other two gallium−phosphorus molecules which have butterfly-shaped rings, $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaPPh_2]_2$.[8] The Ga−P bond distances of 2.463(3) and 2.476(3) Å in molecule A and 2.465(3) and 2.463(3) Å in molecule B are within the the range of those observed for other compounds with bulky substituents on phosphorus, 2.468(4)−2.483(5) Å in $[(n\text{-}Bu_2)_2GaP(t\text{-}Bu)_2]_2$,[10] 2.451(1)

---

[10] Miller, J. E.; Kidd, K. B.; Cowley, A. H.; Jones, R. A.; Ekerdt, J. G.; Gysling, H. J.; Wernberg, A. A.; Blanton, T. N *Chem. Mater.* **1990**, *2*, 589.

Å in $[(t\text{-Bu}_2)_2GaP(H)(C_5H_9)_2]_2$.[11] Thus, the bulky cyclohexyl groups which are bonded at their equatorial positions do not appear to have any unusual effect on the structure of the molecule.

The compound $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$ has the same degree of association in solution as it has in the solid state. Cryoscopic molecular weight studies in benzene lead to an observed degree of association of 2.1. The absence of a concentration dependence for the data further confirms the presence of only dimeric species in solution. Thus, the presence of two bulky cyclohexyl groups is insufficient for the length of the gallium−phosphorus bond to destabilize the dimer in solution and form monomers. The $^{31}P\{^1H\}$ NMR spectrum has only one concentration-independent line at a chemical shift of −15.43 ppm, a value which is very different than those observed for $[(Me_3CCH_2)_2GaP(H)(C_6H_{11})]_2$, −63.6 and −73.3 ppm. The ^1H NMR spectrum is similar to that observed for other gallium−phosphorus dimers and needs no further discussion.

Experimental Section

All compounds were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting compounds $Ga(CH_2CMe_3)_3$,[6] $Ga(CH_2CMe_3)_2Cl$,[6] and $Ga(C_5H_5)_3$[7] were prepared by literature methods. The phosphines were purchased from Strem Chemicals, Inc. and were purified by vacuum distillation before use. The reagent $LiP(C_6H_{11})_2$ was prepared by deprotonating the parent phosphine with Li(*n*-Bu) in hexane. Solvents were dried by conventional procedures. Elememental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or by E+R Microanalytical Laboratory, Corona, NY. The ^1H NMR spectra were recorded either at 300 MHz by using a Varian Gemini-300 spectrometer or at 400 MHz by using a Varian VXR-400 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at 0.00 and C_6H_6 at 7.15 ppm. The ^{31}P NMR spectra were recorded at 161.9 MHz by using the Varian VXR-400 specrometer and are referenced to 85% H_3PO_4 at 0.00 ppm. The ^{13}C NMR spectra were recorded at 75 MHz by using the Varian Gemini-300 spectrometer and are referenced to benzene-d_6 at 128.0 ppm. Standard abbreviations are used to report the multiplicites of the lines. All samples for the NMR spectra were contained in flame-sealed NMR tubes. Infrared spectra were recorded as Nujol mulls between KBr plates with a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with standard abbreviations. Melting points were observed in sealed capillaries and are uncorrected. Molecular weights were measured cryscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.[12]

Synthesis of $(Me_3CCH_2)_2GaPEt_2$ by a Cyclopentadiene Elimination Reaction. The synthesis of $(Me_3CCH_2)_2GaPEt_2$ was also achieved by first reacting 0.970 g (3.42 mmol) of $Ga(CH_2CMe_3)_3$with 0.454 g (1.71 mmol) of $Ga(C_5H_5)_3$ in 30 mL of pentane. After this reaction mixture had stirred for 1 h at room temperature, a solution of 0.463 g (5.14 mmol) of $HPEt_2$ in pentane was added. This mixture was stirred for an additional 18 h, and then all of the compounds volatile at room temperature were removed by vacuum distillation. The resulting brown oil was recrystallized from pentane at −15 °C. The final product $(Me_3CCH_2)_2GaPEt_2$ (0.711 g, 2.36 mmol, 46% yield based on total mmol of gallium) was isolated as colorless crystals. The high solubility of $(Me_3CCH_2)_2GaPEt_2$ in pentane served to lower the observed yield. The compound $(Me_3CCH_2)_2GaPEt_2$ was also observed to sublime at 70 °C under high vacuum. Mp: 101−103 °C. ^1H NMR (C_6D_6): δ 1.00 (p, $^3J_{PCCH} = {}^2J_{HCH} = 6.8$ Hz, 3.1 H, $-CH_3$), 1.06 (t, $^3J_{PGaCH} = 3.4$ Hz, 2.0 H, $Ga-CH_2-$), 1.23 (s, 8.3 H, $-CMe_3$), 1.73 (qt, $^2J_{HCH} = 7.6$ Hz, $^2J_{PCH} = 2.3$ Hz, 2.2 H, $P-CH_2-$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −50.08 (s). Anal. Calcd: C, 55.84; H, 10.71. Found: C, 55.88; H, 10.80. Cryoscopic molecular weight, benzene solution, fw 301.10 (observed molality, observed mol wt, association): 0.08644, 617, 2.05; 0.0488, 618, 2.05; 0.0389, 621, 2.06. IR (Nujol mull, cm^{-1}): 3175 (w), 2728 (w), 2700 (w), 1415 (m), 1233 (s), 1221 (s), 1128 (m), 1102 (m), 1099 (sh), 1035 (s), 1017 (sh), 1010 (s), 997 (s), 970 (m), 963 (m), 928 (m), 906 (m), 845 (w), 817 (vw), 752 (s), 743 (vs), 726 (vs), 719 (sh), 674 (vs), 600 (vs), 451 (vs), 395 (m), 328 (vw), 283 (m), 258 (m).

Synthesis of $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$ by a Cyclopentadiene Elimination Reaction. After a flask was charged with 1.25 g (4.42 mmol) of $Ga(CH_2CMe_3)_3$, 0.586 g (2.21 mmol) of $Ga(C_5H_5)_3$, and 20 mL of pentane, the resulting solution was stirred for 1 h. Then, a preweighed sample of $H_2P(C_6H_{11})$ (0.771 g, 6.64 mmol) dissolved in 10 mL of pentane and contained in a small tube was added to the flask. The reaction mixture was stirred for 18 h at ambient temperature. After the pentane was removed by vacuum distillation, the resulting tan solid was washed with 10 mL of pentane at 0 °C to leave a colorless solid, which was identified as $(Me_3CCH_2)_2GaP(H)(C_6H_{11})$ (1.519 g, 4.643 mmol, 70.0% yield). This product was, in turn, recrystallized from pentane at 0 °C. Mp: 204−210 °C. ^1H NMR (C_6D_6, see Results and Discussion): δ 0.99−1.11 (mbr, C_6H_{11}), 1.13, 1.14, 1.18 (s, $-CH_2-$), 1.24, 1.27 (s, CMe_3), 1.32, 1.36 (s, C_6H_{11}), 1.42 (s, C_6H_{11}), 1.54, 1.58 (s, C_6H_{11}), 1.94 (br, C_6H_{11}), 2.02, 2.06 (s, C_6H_{11}), 2.99 (dd, $^1J_{PH} = 279$ Hz, $^3J_{HPGaP} = 10.4$ Hz, $P-H$), 3.43 (dd, $^1J_{PH} = 306$ Hz, $^3J_{HPGaP} = 9.6$ Hz, $P-H$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.38 (s, $-CH_2$), 27.08 (s, $-CH_2$), 31.01, 31.18, 31.44, 31.48, 32.44, 32.47, 32.59, 32.67 (s, C_6H_{11}), 34.10 (s, $-Me_3$), 34.30 (s, $-Me_3$), 36.02 (s, $-C-$), 36.23 (s, $-C-$), 39.12 (t, $^1J_{PC} = 7.5$ Hz, $P-C$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −63.60 (s, 1.0), −73.26 (s, 1.1). ^{31}P NMR (C_6D_6): δ -63.60 (dd, $^1J_{PH} = 308$ Hz, $^3J_{PGaPH} = 9.4$ Hz), −73.26 (dd, $^1J_{PH} = 280$ Hz, $^3J_{PGaPH} = 10.6$ Hz). ^{31}P NMR (CD_2Cl_2): δ −63.73 (s, 1.0), −73.48 (s, 1.2). Anal. Calcd: C, 58.74; H, 10.61. Found: C, 58.51; H, 10.59. IR (Nujol mull, cm^{-1}): 2310 (w), 1354 (vs), 1340 (m), 1287 (w), 1262 (w), 1232 (m), 1224 (sh), 1170 (w), 1130 (m), 1114 (m), 1100 (m), 1068 (vw), 1039 (vw), 1012 (w), 996 (m), 888 (m), 880 (w), 820 (m), 805 (m), 742 (w), 712 (vs), 680 (w), 607 (m), 585 (sh), 456 (w), 446 (w), 350 (w), 290 (w).

Synthesis of $(Me_3CCH_2)_2GaP(C_6H_{11})_2$ by a Metathesis Reaction. A side-arm dumper charged with 1.07 g (5.26 mmol) of $LiP(C_6H_{11})_2$ was attached to a flask which contained 1.30 g (5.26 mmol) of $Ga(CH_2CMe_3)_2Cl$ and 30 mL of Et_2O. After the solution of the gallium reagent was cooled to 0 °C, the $LiP(C_6H_{11})_2$ was added. A colorless precipitate formed with 20 min. The ice bath was removed, and the mixture was stirred for 18 h as it warmed to room temperature. After the ether was separated by vacuum distillation, the product was extracted four times with 30 mL of pentane each. A final washing of the product with 10 mL of pentane at −78 °C left 1.82 g (4.44 mmol, 84.4% yield) of $(Me_3CCH_2)_2GaP(C_6H_{11})_2$. Crystals suitable for an X-ray structural study were grown by the slow evaporation of a methylcyclohexane solution in the drybox. Mp: 248−250 °C. ^1H NMR (C_6D_6): δ 1.09−1.16 (br, 1.1 H, C_6H_{11}), 1.21 (t, $^3J_{PGaCH} = 3.6$ Hz, 2.0 H, $-CH_2-$), 1.27 (s, 0.9 H, C_6H_{11}), 1.32 (s, 9.0 H, $-CMe_3$), 1.62 (t, $^2J_{HCH} = 10.5$ Hz, 2.9 H, C_6H_{11}), 1.75 (d, $^2J_{HCH} = 12.1$ Hz, 2.0 H, C_6H_{11}), 2.14 (d, $^2J_{HCH} = 12.1$ Hz, 2.0 H, C_6H_{11}), 2.29 (t, $^2J_{HCH} = 12.0$ Hz, 0.8 H, C_6H_{11}). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −15.43 (s). Anal.

---

(11) Heaton, D. E.; Jones, R. A.; Kidd, K. B.; Cowley, A. H.; Nunn, C. M. *Polyhedron* **1988**, *7*, 1901.

(12) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986; p 38.

(13) Sheldrick, G. M. *SHELX76, a system of computer programs for X-ray structure determination as locally modified*; University of Cambridge: Cambridge, England, 1976.

(14) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

Table 3. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$

	$[(Me_3CCH_2)_2GaPEt_2]_2$	$[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$
mol form	$Ga_2P_2C_{28}H_{64}$	$Ga_2P_2C_{44}H_{88}$
color/shape	colorless/parallelepiped	colorless/parallelepiped
mol wt	602.21	818.58
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
temp, °C	20	20
a, Å	16.524(2)	15.280(2)
b, Å	10.225(2)	18.216(3)
c, Å	20.677(4)	19.046(7)
α, deg		105.63(2)
β, deg	95.25(1)	102.54(2)
γ, deg		97.54(1)
$Å^3$	3478.9	4880.9
Z	4	4
D_{calcd}, g cm^{-1}	1.15	1.11
μ_{calcd}, cm^{-1}	17.4	12.5
diffractometer/scan	Enraf-Nonius CAD4/$\omega-2\theta$	
range of relative transmission factors, %	94/100%	
radiation, graphite monochromator	Mo Kα ($\lambda = 0.710\,73$ Å)	Mo Kα ($\lambda = 0.710\,73$ Å)
max cryst dimens, mm	$0.20 \times 0.25 \times 0.28$	$0.08 \times 0.15 \times 0.20$
no. of reflns measd	3349	17 156
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of h,k,l	+19,+12,±24 (except $h + k = 2n + 1$)	+18,±21,±22
no. of reflns obsd [$F_o \geq 5\sigma(F_o)$]	2035	8503
computer programs	SHELX[13]	SHELX[13]
structure solution	SHELXS[14]	SHELXS[14]
weights	$[\sigma(F_o)^2 + 0.0005F_o^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF	0.71	2.36
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.037	0.079
R_w	0.046	0.080
largest feature final diff map	0.3 e$^-$ Å^{-3}	0.8 e$^-$ Å^{-3}

Calcd: C, 64.56; H, 10.84. Found: C, 64.83; H, 10.79. Cryoscopic molecular weight, benzene solution, fw 408 (observed molality, observed mol wt, association): 0.0455, 863, 2.11; 0.0365, 868, 2.12; 0.0292, 857, 2.09. IR (Nujol mull, cm^{-1}): 2730 (w), 2700 (w), 2665 (w), 1352 (s), 1324 (m), 1292 (sh), 1287 (m), 1262 (m), 1254 (sh), 1236 (s), 1219 (s), 1192 (m), 1168 (m), 1130 (m), 1125 (m), 1106 (m), 1067 (w), 1042 (w), 1022 (sh), 1010 (m), 998 (s), 930 (w), 908 (m), 892 (sh), 882 (s), 847 (m), 842 (sh), 745 (m), 733 (m), 695 (vs), 664 (sh), 593 (s), 577 (sh), 509 (w), 487 (vw), 452 (m), 385 (w), 300 (w), 280 (w).

X-ray Data Collection, Structure Determination, and Refinement. (a) $[(Me_3CCH_2)_2GaPEt_2]_2$. A transparent single crystal of the 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 $C2/c$ or acentric Cc from the systematic absences. Subsequent solution and refinement of the structure was carried out by using the centric space group $C2/c$. A summary of the data collection parameters is given in Table 3. Least-squares refinement with isotropic thermal parameters led to $R = 0.072$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atoms 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 $R = 0.037$ and $R_w = 0.046$.

(b) $[(Me_3CCH_2)_2GaP(C_6H_{11})_2]_2$. The compound was mounted in a thin-walled capillary under argon. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Solution and refinement were successfully carried out in $P\bar{1}$. A summary of data collection parameters is given in Table 3. After least-squares refinement with isotopic thermal parameters and no disorder led to $R = 0.111$, it was obvious that extremely high thermal motion was interferring with the refinement of the structure. It was not possible to refine a disorder model for the methyl groups which appear to be freely rotating, however, disorder at C(1) and at the cyclohexyl group C(39)−C(44) in molecule A and at C(45), and C(59) in molecule B was resolved. The disorder at C(1), C(45) and C(55) involves fractional displacement of these CH_2 groups, and C(1)′, C(45)′, and C(55)′ were included at 50% occupancy. Any disorder in the attached CMe_3 groups was not resolvable. Conformational disorder exists in the cyclohexyl group C(39)−C(44). Atoms C(39) and C(44) are common to both orientations. C(40)−C(43) were each resolved into two positions refined in alternate least-squares cycles at 50% occupancy each. The conformation without primes C(39)−C(44) results in molecules A and B having essentially the same overall structure. In this orientation three of the cyclohexyl groups have the same general orientation to the Ga_2P_2 ring, whereas one is twisted by approximately 90°. In the disorder model containing C(39) and C(40)′−C(43)′, two of the cyclohexyl groups are twisted. Refinement of this structure in the acentric space group $P1$ was unsuccessful. The disorder was still apparent, and there were high correlations between atoms that would be related by the center of inversion in $P1$. Due to the high thermal motion and disorder, the hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms (except for the methyl groups) with anisotropic temperature factors led to the final values $R = 0.079$ and $R_w = 0.080$.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms and ORTEP diagrams of $[(Me_3CCH_2)_2GaPEt_2]_2$ and $[Ga(CH_2CMe_3)_2P(C_6H_{11})_2]_2$ (25 pages). Ordering information is given on any current masthead page.

OM970090P