Note

Trimethylgallium based phosphinogallanes. Synthesis and molecular structure of $[Me_2Ga–P(SiMe_3)_2]_2$

Mary D.B. Dillingham, Jaye A. Burns,
Jameica Byers-Hill, Kevin D. Gripper,
William T. Pennington
and Gregory H. Robinson*
Howard L Hunter Chemistry Laboratory, Department of Chemistry, Clemson University, Clemson, SC 29634-1905 (USA)

(Received August 27, 1993; revised October 20, 1993)

Abstract

The sterically demanding phosphinogallane $[Me_2Ga–P(SiMe_3)_2]_2$, prepared from reaction of trimethylgallium and tris(trimethylsilyl)phosphine in toluene, has been characterized by partial elemental analyses, ^1H NMR and single crystal X-ray diffraction. The title compound crystallizes in the space group $P\bar{1}$ (No. 2) with unit cell dimensions $a=9.711(1)$, $b=9.857(1)$, $c=9.211(1)$ Å, $\alpha=99.62(1)$, $\beta=116.25(1)$, $\gamma=76.28(1)°$, $V=766.3$ Å^3 and $D_{calc}=1.20$ g cm^{-1} for $Z=1$ Refinement converged at $R=0.037$, $R_w=0.046$, based on 1606 observed reflections with intensities $I>3\sigma(I)$ The independent Ga–P distance was determined to be 2.456(1) Å Pyrolysis of the dimer did not afford higher order phosphinogallanes.

Key words. Crystal structures; Gallium complexes; Alkyl complexes, Phosphinogallane complexes

Introduction

The past decade has arguably been the most productive in main group chemistry. Certainly, this case may be persuasively made for the Group 13 (III) metals as a wealth of seminal discoveries have been forged in recent years. While the efforts of this laboratory have largely concerned the coordination chemistry of aluminum [1], recently our attention has shifted toward the corresponding chemistry of the heavier Group 13 metals such as gallium and indium. While phosphido complexes of gallium and indium have been shown to be advantageous in the quest toward a host of promising materials [2], the literature reveals a relative paucity of such studies based upon the simple trialkyls such as trimethylgallium and trimethylindium. To this end, and in an effort to examine the ramifications of sterically demanding ligands on this chemistry, we endeavored to examine the organometallic chemistry of trimethylgallium relative to phosphine steric loading. Herein we report the synthesis and structure of the novel dimeric phosphinogallane $[Me_2Ga-P(SiMe_3)_2]_2$ (**I**), isolated from reaction of Me_3Ga with the sterically demanding phosphine tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$, in toluene. The formation of **I** is facilitated by an intriguing $SiMe_4$ elimination

Experimental

Synthesis

Tris(trimethylsilyl)phosphine was prepared by the method given by Uhl and co-workers [3]. Inside the drybox Me_3Ga (5.0 mmol, 0.50 ml) was combined with $P(SiMe_3)_3$ (5.0 mmol, 1.25 g) and toluene (20 ml) in a reaction tube. The homogeneous solution was allowed to stand at room temperature for 4 h and then placed in the freezer. After concentrating the solution, further cooling afforded colorless, rectangular, X-ray quality crystals of **I** (0.97 g, 70% yield) (m.p. = 160 °C). ^1H NMR ($CDCl_3$): δ 0.113 (t, 12H, $GaCH_3$); 0.053 (t, 36H, $SiCH_3$). *Anal.* (E+R Laboratories, Corona, NY) Calc. for $C_{16}H_{48}Si_4P_2Ga_2$: C, 34.67; H, 8.73. Found: C, 34.37; H, 8.11%.

Crystal data

X-ray intensity data were collected on a Nicolet P3 diffractometer using graphite monochromatic Mo Kα radiation ($\lambda=0.71073$ Å) using the ω–2θ scan technique. The non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located by standard difference techniques and were included in the structure factor calculation at idealized positions (d(C–H)$=0.96$ Å). The structure was solved by direct methods and refined, using SHELXTL [4]. **I** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell dimensions $a=9.711(1)$, $b=9.857(1)$, $c=9.211(1)$ Å, $\alpha=99.62(1)$, $\beta=116.25(1)$, $\gamma=76.28(1)°$, $V=766.3$ Å^3 and $D_{calc}=1.20$ g cm^{-1} for $Z=1$. Refinement converged at $R=0.037$, $R_w=0.046$, based on 1606 observed reflections with intensities $I>3\sigma(I)$. The X-ray crystal structure of $[Me_2Ga-P(SiMe_3)_2]_2$ is given in Fig. 1. Final atomic coordinates are provided in Table 1 while bond distances and angles are given in Table 2.

---

*Author to whom correspondence should be addressed.

SSDI 0020-1693(93)03738-V

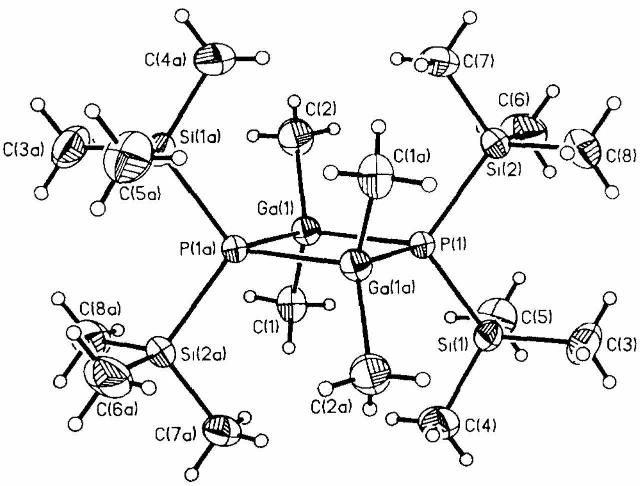

Fig. 1 Molecular structure of $[Me_2Ga–P(SiMe_3)_2]_2$.

TABLE 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Me_2Ga–P(SiMe_3)_2]_2$

	x	y	z	U_{eq}[a]
Ga(1)	1354(1)	795(1)	−198(1)	45(1)
P(1)	1287(1)	−1553(1)	306(1)	39(1)
Si(1)	1586(2)	−3186(1)	−1620(2)	50(1)
Si(2)	3104(2)	−2260(2)	2754(2)	52(1)
C(1)	1384(6)	844(6)	−2326(7)	62(3)
C(2)	2951(7)	1698(6)	1649(8)	76(3)
C(3)	1696(9)	−4962(6)	−1114(8)	84(4)
C(4)	−78(8)	−2825(7)	−3616(7)	92(4)
C(5)	3417(8)	−3136(8)	−1782(9)	91(4)
C(6)	5083(7)	−2577(9)	2812(9)	99(4)
C(7)	2977(7)	−871(6)	4338(6)	74(3)
C(8)	2733(10)	−3875(7)	3221(8)	101(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 2 Bond distances and angles for $[Me_2Ga–P(SiMe_3)_2]_2$

Distances Å			
Ga(1)–P(1)	2.456(1)	Ga(1)–C(1)	1.981(7)
Ga(1)–C(2)	1.977(5)	P(1)–Si(1)	2.258(2)
P(1)–Si(2)	2.259(2)	Si(1)–C(3)	1.853(7)
Si(1)–C(4)	1.854(5)	Si(1)–C(5)	1.861(9)
Si(2)–C(6)	1.850(7)	Si(2)–C(7)	1.852(6)
Si(2)–C(8)	1.867(9)		
Angles (°)			
P(1)–Ga(1)–C(1)	112.5(2)	P(1)–Ga(1)–C(2)	113.2(2)
C(1)–Ga(1)–C(2)	114.5(3)	P(1)–Ga(1)–P(1A)	88.0(1)
C(1)–Ga(1)–P(1A)	112.3(2)	C(2)–Ga(1)–P(1A)	113.7(2)
Ga(1)–P(1)–Si(1)	112.0(1)	Ga(1)–P(1)–Si(2)	113.5(1)
Si(1)–P(1)–Si(2)	108.2(1)	Ga(1)–P(1)–Ga(1A)	92.0(1)
Si(1)–P(1)–Ga(1A)	117.3(1)	Si(2)–P(1)–Ga(1A)	113.2(1)
P(1)–Si(1)–C(3)	110.9(3)	P(1)–Si(1)–C(4)	110.1(2)
C(3)–Si(1)–C(4)	109.0(3)	P(1)–Si(1)–C(5)	109.7(2)
C(3)–Si(1)–C(5)	108.8(4)	C(4)–Si(1)–C(5)	108.3(4)
P(1)–Si(2)–C(6)	110.3(3)	P(1)–Si(2)–C(7)	108.8(2)
C(6)–Si(2)–C(7)	109.2(3)	P(1)–Si(2)–C(8)	111.0(2)
C(6)–Si(2)–C(8)	110.1(4)	C(7)–Si(2)–C(8)	107.3(3)

Results and discussion

It is significant that a number of phosphinogallanes have concerned sterically demanding gallium alkyls. The synthesis of $[Neo_2Ga–PPh_2]_2$ [5] (Ga–$P_{bridging}$: 2.457(9) and 2.469(9); Ga–$P_{terminal}$: 2.351(1) Å) from the Ga–P trimer $[Neo(Cl)Ga–PPh_2]_3$ (Neo = neopentyl, $-CH_2$-CMe_3) represents an interesting example. Furthermore, the novel trimer $[t\text{-}Bu_2Ga(\mu\text{-}PH_2]_3$ [6] as prepared from reaction of the sterically demanding $t\text{-}Bu_3Ga$ with PH_3 (Ga–P: 2.439(3) Å) is intriguing. In addition, as evidenced by the preparation of the monomers $Ph_2(Cl)Ga–P(SiMe_3)_3$ (2.45(2) Å) and $Ph_3Ga–P$-$(SiMe_3)_3$, (2.539(6) Å) and the mixed-bridged four-membered ring complex $[Ph_2Ga(Cl)(PSiMe_3)_2GaPh_2]$ (Ga–P: 2.389(3) Å) [7], sterically demanding phosphines such as tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$, have recently been brought to the fore of Group 13 chemistry [8]. Indeed, the preparation of the gallium phosphide molecular precursor $[Cl_2Ga–P(SiMe_3)_2]_2$ [9], lends valuable perspective. Reaction of $GaCl_3$ with $P(SiMe_3)_3$ affords the dimer with concomitant dehalosilylation elimination of Me_3SiCl. The Ga_2P_2 ring is planar with Ga–P distances of 2.378(2) and 2.380(2) Å. It is interesting to note that elimination of Me_3SiCl has also been observed in the preparation of $[(Me_3SiCH_2)_2In–P(SiMe_3)_2]_2$ from reaction of $(Me_3SiCH_2)_2InCl$ with $P(SiMe_3)_3$ [10, 11]. In addition, a related sterically demanding phosphinogallane, $[Me_2Ga–P(t\text{-}Bu)_2]_2$ has been prepared from reaction of $GaCl_3$, with $(t\text{-}Bu)_2PLi$ in the presence of Li(t-Bu) [12].

In notable contrast, the preparation of **I**, and indeed the preparation of the indium analog and demonstrated indium phosphide molecular precursor $[Me_2In–P(SiMe_3)_2]_2$, (**II**) [13]*, isolated from the corresponding reaction involving Me_3In, suggests that dimeric phosphinogallanes and phosphinoindanes need not necessarily proceed via dehalosilylation elimination involving Me_3SiCl, but alternatively, may also be reasonably approached from reaction of Me_3M (M = Ga, In) with $P(SiMe_3)_3$ (eqn. (1)).

$$Me_3M + P(SiMe_3)_3 \longrightarrow \tfrac{1}{2}[Me_2M–P(SiMe_3)_2]_2 + SiMe_4 \quad (1)$$

---

*Although the dimeric nature of $[Me_2In–P(SiMe_3)_2]_2$ was confirmed by single crystal X-ray diffraction in this study, only gross structural aspects of the compound were reported as crystallographic and all metrical structural details were deposited as Supplementary material

It is important to note that while $SiMe_4$ elimination from indium–silylphosphine systems has been previously observed, for example in the preparation of $[(Me_3SiCH_2)_2In–P(H)t\text{-}Bu]_2$ [14] and $[(Me_3SiCH_2)_2In–P(H)Ada]_2$ [15], these systems, significantly, concerned primary phosphines. As an interesting aside, an independent preparation* and single crystal X-ray diffraction examination of **II** performed in this laboratory [16] confirms that the indium derivative is isostructural with **I**. It is noteworthy that **I** and **II**, unlike dimeric aminoalanes or aminogallanes, do not afford higher-order phosphinogallanes (i.e. trimer or tetramer) upon further pyrolysis.

The title compound resides about a perfectly planar Ga_2P_2 four-membered ring with P–Ga–P and Ga–P–Ga endocyclic bond angles of 88.0(1) and 92.0(1)°, respectively. With exocyclic Si–P–Si and C–Ga–C bond angles of 108.2(1) and 114.5(3)°, respectively, the coordination about the phosphorus and gallium atoms may be described as distorted tetrahedral. The independent Ga–P distance of 2 456(1) Å of **I** is unremarkable as it falls within the expected range of reported Ga–P interactions.

The In–P distances in **II** were determined to be 2.623(1) and 2.630(1) Å. For comparison, the In–P distances in $[(Me_3SiCH_2)_2In–P(SiMe_3)_2]_2$ were found to be 2.656(2) and 2.654(2) Å, while those for the corresponding mixed P–Cl bridged compound, $[(Me_3SiCH_2)_2In–P(SiMe_3)_2In(CH_2SiMe_3)_2Cl]$, were shown to be 2.605(2) and 2.601(3) Å [13]. Thus, the In–P bond distances observed in **II** may be regarded among the shortest such interactions reported for a phosphinoindane containing an In_2P_2 four-membered ring. As the In–In bond distance in tetrakis[bis(trimethylsilyl)methyl]diindane, $[(Me_3Si)_2HC]_2In–In[CH(SiMe_3)_2]_2$, is 2.828 Å [17], the In · · In approach of 3.809(1) Å in **II** is not indicative of significant metal–metal interaction. Correspondingly, the Ga · · Ga approach of 3.535(1) Å in **I** does not suggest metal–metal bonding as a Ga–Ga distance of 2.541(1) Å was reported for $[(Me_3Si)_2HC]_2Ga–Ga[CH(SiMe_3)_2]_2$ [18].

Trimethylgallium and -indium represent a potentially fruitful avenue for phosphinogallanes and -indanes particularly with sterically demanding phosphines. Studies addressing other aspects of this area are forthcoming.

Supplementary material

A summary of data collection and refinement, plots of molecule, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (16 pages) are available from the authors upon request.

Acknowledgement

We are grateful to the National Science Foundation for support of this work to G.H.R. (CHE-9100518).

References

1 G H Robinson (ed.), *Coordination Chemistry of Aluminum*, VCH, New York, 1993

2 A H. Cowley and R A Jones, *Angew Chem, Int. Ed Engl.*, *28* (1989) 1208

3 G Becker, H. Schmidt, G Uhl and W Uhl, *Inorg Synth*, *27* (1990) 243

4 G M Sheldrick, *SHELXTL*, crystallographic computing system, Nicolet Instruments Division, Madison, WI, 1986

5 O.T. Beachley, Jr and J.D Maloney, *Organometallics, 12* (1993) 229

6 A.H Cowley, P.R Harris, R.A. Jones and C M Nunn, *Organometallics, 10* (1991) 652

7 R L Wells, S R Aubochon, M F. Self, J P Jasinski, R.C. Woudenberg and R J. Butcher, *Organometallics, 11* (1992) 3370

8 R L. Wells, A.T McPhail, L J. Jones and M F Self, *Organometallics, 11* (1992) 2694

9 R L. Wells, M.F. Self, A T. McPhail and S.R. Aubochon, *Organometallics, 12* (1993) 2832.

10 R.L Wells, A.T McPhail and M.F. Self, *Organometallics, 11* (1992) 221

11 T. Douglas and K H. Theopold, *Inorg Chem., 30* (1991) 594.

12 A M. Arif, B.L. Benac, A H. Cowley, R Geerts, R.A. Jones, K.B. Kidd, J.M Power and S.T. Schwab, *J Chem. Soc, Chem Commun*, (1986) 1543.

13 S.M Stuczynski, R.L. Opila, P. Marsh, J G. Brennan and M L Steigerwald, *Chem Mater., 3* (1991) 379

14 U Dembowshi, M Noltemeyer, W. Rockensub, M. Stuke and H W Roesky, *Chem Ber, 123* (1990) 2335.

15 U Dembowshi, H W. Roesky, E. Pohl, R Herbst-Irmer, D Stalke and G M Sheldrick, *Z Anorg Allg Chem*, *611* (1992) 92

16 J.A. Burns, J. Byers Hill, M.D.B. Dillingham, K.D. Gripper, W.T. Pennington and G H. Robinson, unpublished results.

17 W Uhl, M Layh and W. Hiller, *J Organomet Chem*, *368* (1989) 139

18 W. Uhl, M. Layh and T. Hildenbrand, *J Organomet Chem*, *364* (1989) 289

---

*Colorless, rectangular, X-ray quality crystals of **II** were isolated under conditions similar to those employed for **I**: (0 90 g, 90% yield) (m.p. = 122 °C (dec.)). ^1H NMR ($CDCl_3$): δ −0 111 (t, 12H, InCH_3); 0.285 (t, 36H, SiCH_3). *Anal.* (E + R Laboratories, Corona, NY) Calc. for $C_{16}H_{48}Si_4P_2In_2$. C, 29.81; H, 7.51. Found C, 29.53; H, 7.55%.