75

ANGEWANDTE
CHEMIE

103. Jahrgang 1991
Heft 10
Seite 1353–1354

International Edition in English

Reprint

The Interaction of Tri-*tert*-butylgallium with White Phosphorus: Isolation of an Unusual Gallium Phosphorus Cluster**

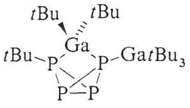
By *Michael B. Power* and *Andrew R. Barron**

Despite the vast quantity of literature concerning compounds containing both group 13 and 15 elements, and their proposed relevance to electronic materials,[1] there has been surprisingly little variation in the chemistry of these compounds since they were first reported nearly 30 years ago.[2] Thus, the vast majority of the compounds fall into one of two classes of compound, i.e., $[MR_x(ER'_2)_{3-x}]_n$ (x = 0, 1, 2 and n = 1, 2, 3)[3] and $(RMER)_n$ ($n = 2 \rightarrow \infty$)[4] where M is a group 13 metal, Al, Ga, or In and E is one of the group 15 elements N, P, As, or Sb. Two notable exceptions are the unusual gallium-arsenic and gallium-phosphorus clusters reported by the groups of *Wells* et al.[5] and *Power* et al.,[6] $[(GaR_2)(GaR)_4(AsHPh)(AsPh)_6]$ and $[Ga(GaR)_3(PR')_4\text{-}(PHR')]$ ($R = CH_2SiMe_3$, R′ = 1-adamantyl, Ar = 2,4,6-$i\text{Pr}_3C_6H_2$).

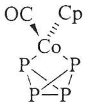
In an effort to develop new classes of mixed 13/15 compounds we have investigated the reaction of group 13 alkyls with elemental phosphorus. The results for $Ga\textit{t}Bu_3$ are presented herein.

The reaction of white phosphorus, P_4, with two molar equivalents of $Ga\textit{t}Bu_3$,[7] in pentane at room temperature, affords a colorless solid with a composition corresponding to $Ga_2P_4\textit{t}Bu_6$ **1**. The medium-resolution mass spectrum (70 eV, CI, NH_3) of **1** exhibits a fragmentation pattern *m*/*z* consistent with loss of *t*Bu (*m*/*z* = 566) and $Ga\textit{t}Bu_3$ (*m*/*z* = 365).

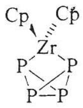
The ^1H and $^{13}C\text{-}\{^1H\}$-NMR spectra of **1**[8] indicate the presence of three different *tert*-butyl environments with an integrated ratio of 3:2:1, the latter showing coupling to a single phosphorus atom. The $^{31}P\text{-}\{^1H\}$-NMR spectrum of **1**[8] consists of three signals which exhibit P–P one-bond coupling to give two triplets and a doublet of doublets. The one-bond connectivity of the phosphorus atoms is confirmed by the homonuclear 2D-^{31}P-NMR-COSY[9] spectrum. The shift of the downfield triplet ($\delta = -50.73$) is close to that observed for "*t*BuP" fragments in the polycyclodiphosphanes $\textit{t}Bu_6P_8$ ($\delta = -45$),[10] while the two upfield signals ($\delta = -226.81$ and -327.43) are indicative of a tetrahedrane type phosphorus environment, and may be compared with those for the transition metal complexes **2** ($\delta = -258.2$, -335.9, and -376.9),[11] **3** ($\delta = 166.1$ and -206.5),[12] and **4** ($\delta = -247.0$).[13]



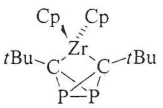
1



2



3



4

The similarity of the ^{31}P-NMR spectrum for **1** to that of **2** suggests that they are structurally related, however, since the structure of **1** could not be established unequivocally from NMR spectroscopy, an X-ray crystal structure analysis was performed,[14] the result of which is presented in Figure 1. The X-ray structure is entirely consistent with analytical and spectroscopic data. All the P–P distances [2.197(2)–2.214(2) Å] are consistent with that of a P–P single bond. The Ga(1)–P(1) and Ga(1)–P(4) distances, 2.515(2) and 2.476(2) Å respectively, are towards the long end of the range previously observed for Ga–P bonds, 2.370(3)–2.475(4) Å,[6, 15] consistent with the strain imposed by the small P(1)–Ga(1)–P(4) angle, 68.8(1)°. The dative P(4)–Ga(2) bond [2.619(2) Å] is significantly longer than those associated with the P–Ga–P bridge, and is presumably a result of the steric crowding at Ga(2) due to the three *tert*-butyl ligands.

Since little is known about ring opening reactions of white phosphorus with Lewis acids we can, at present, only speculate as to how **1** is formed. Presumably the initial reaction

---

[*] Prof. Dr. A. R. Barron, Dr. M. B. Power
Department of Chemistry
Harvard University
Cambridge, MA 02138 (USA)

[**] This work was supported by the US-Petroleum Research Fund.

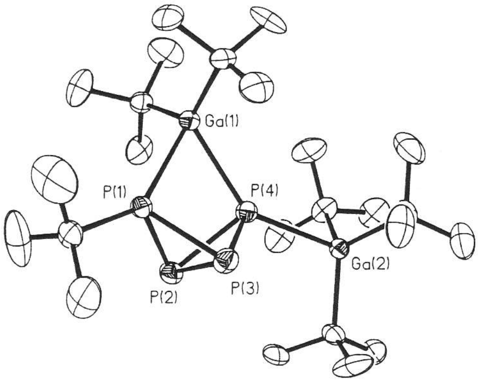


Fig. 1. Structure of **1** in the crystal (ORTEP). Important bond lengths and angles, see text.

involves the addition of a Ga–C bond across one of the P–P bonds in P_4 since a related addition of alkyllithium reagent across P_4 has previously been described.[16] Finally, we note that thermolysis (75–80 °C in C_6D_6) of **1** results in the liberation of Ga*t*Bu$_3$ and the decomposition of the remaining GaP$_4$*t*Bu$_3$ moiety.

Experimental Procedure

1: Ga*t*Bu$_3$ (3.89 g, 16.13 mmol) in pentane (40 mL) was stirred for 3 to 4 h with P_4 (1.0 g, 8.07 mmol) at room temperature under nitrogen. After all the P_4 had been visibly consumed by the reaction a pale yellow solution resulted. Some solvent was then removed under vacuum (ca. 10 mL), and the resulting solution set aside in the freezer overnight (−25 °C). A large mass of white crystalline material was deposited, which was filtered and dried under vacuum. More crystalline material was obtained from the filtrate. Yield: 4.10 g, 84%. m.p. 120–121 °C.

Received: May 22, 1991 [Z 4641 IE]
German version: *Angew. Chem. 103* (1991) 1403

CAS Registry numbers:
1, 135989-55-8; P_4, 12185-10-3; Ga*t*Bu$_3$, 55681-99-7.

---

[1] For a review, see: A. H. Cowley, R. A. Jones, *Angew. Chem. 101* (1989) 1235; *Angew. Chem. Int. Ed. Engl. 28* (1989) 1208, and references therein.

[2] a) G. E. Coates, J. Graham, *J. Chem. Soc. 1963*, 223; b) O. T. Beachley, Jr., G. E. Coates, *J. Chem. Soc. 1965*, 3241.

[3] a) R. L. Wells, A. P. Purdy, A. T. McPhail, C. G. Pitt, *J. Organomet. Chem. 308* (1986) 281; b) A. M. Arif, B. L. Benac, A. H. Cowley, R. L. Geerts, R. A. Jones, K. B. Kidd, J. M. Power, S. T. Schwab, *J. Chem. Soc. Chem. Commun 1986*, 1543; c) O. T. Beachley, Jr., J. P. Kopasz, H. Zhang, W. E. Hunter, J. L. Atwood, *J. Organomet. Chem. 325* (1987) 69; d) C. G. Pitt, K. T. Higa, A. T. McPhail, R. L. Wells, *Inorg. Chem. 25* (1986) 2483; e) K. M. Waggoner, P. P. Power, *J. Am. Chem. Soc. 113* (1991) 3385.

[4] a) K. M. Waggoner, H. Hope, P. P. Power, *Angew. Chem. 100* (1988) 1765; *Angew. Chem. Int. Ed. Engl. 27* (1988) 1699; b) R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc. 112* (1990) 3660.

[5] R. L. Wells, A. P. Purdy, A. T. McPhail, C. G. Pitt, *J. Chem. Soc. Chem. Commun. 1986*, 487.

[6] K. M. Waggoner, S. Parkin, D. C. Pestana, H. Hope, P. P. Power, *J. Am. Chem. Soc. 113* (1991) 3597.

[7] R. A. Kovar, H. Derr, D. Brandau, J. O. Callaway, *Inorg. Chem. 14* (1975) 2809.

[8] ^{1}H NMR (500 MHz, C_6D_6, TMS ext.): $\delta = 1.36$ (s, 27 H; GaC(CH$_3$)$_3$), 1.26 (s, 18 H; GaC(CH$_3$)$_3$), 0.511 (d, J(P,H) = 13.87 Hz, 9 H; PC(CH$_3$)$_3$); ^{13}C NMR (125.72 MHz, C_6D_6, TMS ext.): $\delta = 40.60$ (d, J(P,C) = 49.55 Hz, P*C*(CH$_3$)$_3$), 33.63 (GaC(*C*H$_3$)$_3$), 31.53 (Ga*C*(CH$_3$)$_3$), 31.08 (GaC(*C*H$_3$)$_3$), 27.93 (d, J(P,C) = 9.05 Hz, PC(*C*H$_3$)$_3$), 27.76 (Ga*C*(CH$_3$)$_3$); ^{31}P-{^{1}H}-NMR (202.40 MHz, C_6D_6, H_3PO_4 ext.): $\delta = -50.73$ (t, J(P,P) = 212.45 Hz, 1 P; P*t*Bu), −226.81 (t, J(P,P) = 205.71 Hz, 1 P; PGa*t*Bu$_3$), −327.43 (overlapping dd, J(P,P) = 207.52 Hz, 209.74 Hz, 2P; P_2P*t*Bu). IR (KBr, Nujol): $\tilde{\nu}$ [cm^{-1}] = 2357 (w), 2165 (w), 1973 (w), 1686 (w), 1164 (s), 1072 (w), 1005 (s), 935 (m), 897 (sh), 850 (w), 805 (s), 725 (m), 685 (w), 597 (m), 568 (w), 526 (m), 398 (m).

[9] a) W. P. Ave, E. Bartholidi, R. R. Ernst, *J. Chem. Phys. 64* (1976) 2229; b) K. Nagayama, A. Kumar, K. Wüthrich, R. R. Ernst, *J. Magn. Reson. 40* (1980) 321.

[10] M. Baudler, J. Hellmann, P. Bachmann, K.-F. Tebbe, R. Fröhlich, M. Fehér, *Angew. Chem. 93* (1981) 415; *Angew. Chem. Int. Ed. Engl. 20* (1981) 406.

[11] O. J. Scherer, M. Swarowsky, G. Wolmershäuser, *Organometallics 8* (1989) 841.

[12] O. J. Scherer, M. Swarowsky, H. Swarowsky, G. Wolmershäuser, *Angew. Chem. 100* (1988) 738; *Angew. Chem. Int. Ed. Engl. 27* (1988) 694.

[13] P. Binger, B. Biedenback, C. Krüger, M. Regitz, *Angew. Chem. 99* (1987) 798; *Angew. Chem. Int. Ed. Engl. 26* (1987) 764.

[14] X-ray structure analysis of **1**: space group $P\bar{1}$, $a = 9.436(4)$, $b = 12.331(4)$, $c = 15.866(4)$, $\alpha = 70.76(2)$, $\beta = 81.21(3)$, $\gamma = 69.95(3)^\circ$, $V = 1635(1)$ Å^3, $\varrho_{calcd} = 1.230$ g cm^{-3}, $\mu(\text{Mo}_{K_\alpha}) = 18.44$ cm^{-1}, 4242 unique reflections, 3342 observed ($I > 4\sigma(I)$), $R = 0.0412$, $R_w = 0.0536$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-15575, the names of the authors, and the journal citation.

[15] A. H. Cowley, P. R. Harris, R. A. Jones, C. M. Nunn, *Organometallics 10* (1991) 652.

[16] R. Riedel, H.-D. Hausen, E. Fluck, *Angew. Chem. 97* (1985) 1050; *Angew. Chem. Int. Ed. Engl. 24* (1985) 1056.