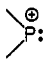
Base-Induced Coordination of a Prototypical Phosphenium Cation to Gallium Trichloride

Neil Burford,* Pierre Losier, Sergey V. Sereda,
T. Stanley Cameron,* and Gang Wu

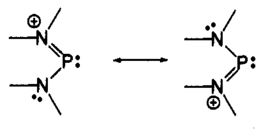
Department of Chemistry, Dalhousie University
Halifax, Nova Scotia B3H 4J3, Canada

Received March 9, 1994

There are numerous examples of phosphenium salts, containing a formally electron deficient, coordinatively unsaturated, cationic phosphorus center **1**.[1] Although these molecular units are considered analogues of carbenes, all isolated examples possess a significant degree of π-donation to the phosphorus center from an electron-rich neighboring atom (or atoms), such as nitrogen in **2**.[2,3] Phosphenium centers that lack such π-interaction have



1



2

not been reported, and synthetic attempts for alkylated derivatives reveal a preference for typical covalent coordination complexes[4] (e.g., $Bu^t_2(Cl)P \rightarrow AlCl_3$)[5] or a cationic coordination complex between a phosphine and a phosphenium center (also referred to as a phosphinophosphonium).[6] Our attempts to study the prototypical phosphenium cation Me_2P^+ have led to the discovery of the ionic material **3**[$GaCl_4$], containing the novel 2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium–gallium trichloride complex cation **3**.

NMR studies of the rapid reaction between chlorodimethylphosphine and gallium trichloride in dichloromethane show essentially quantitative formation of asymmetric P–P bonded products, the nature of which depends upon the stoichiometry.[7,8] The ionic material **3**[$GaCl_4$][9] has been isolated from the equimolar reaction mixture, and the crystal structure,[10] although disordered, conclusively reveals a cation (Figure 1) containing adjacent tetracoordinate phosphorus centers. The structure represents a Me_2PCl moiety (P2) coordinated to a phosphenium moiety Me_2P^+ (P1), which is in turn coordinated to a $GaCl_3$ molecule.[11] The P–P bond length [2.138(7) Å and 2.156(10) Å] is consistent with a diphosphonium structure (2.189 Å).[12]

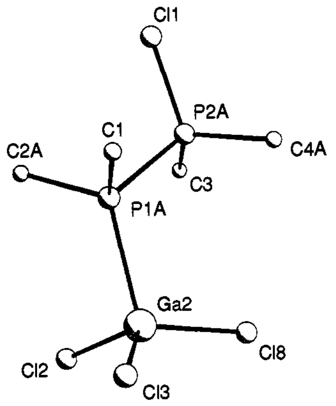


Figure 1. Crystallographic view of cation **3** in one of two disordered positions.

The solid-state ^{31}P CP-MAS NMR spectrum of **3**[$GaCl_4$] exhibits a significantly smaller P–P coupling ($^1J_{PP}$ = 154 Hz) and ^{31}P chemical shift differential ($\delta_{isotropic}$ = 84 ppm, −16 ppm) than the solution NMR spectrum of an equimolar reaction mixture (96 ppm, −28 ppm, $^1J_{PP}$ = 311 Hz) and resembles that of a solution containing an excess of $GaCl_3$ (89 ppm, −16 ppm, $^1J_{PP}$ = 219 Hz). A reaction mixture containing a 2-fold excess of Me_2PCl (99 ppm, −33 ppm, $^1J_{PP}$ = 340 Hz) shows no evidence of free phosphine and is similar to solution spectra of **3**[$GaCl_4$] (98 ppm,

---

(1) Sanchez, M.; Mazieres, M. R.; Lamande, L.; Wolf, R. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; pp 129–148.

(2) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367–382.

(3) Burford, N.; Losier, P.; Bakshi, P. K.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1993**, 201–202. Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434–1439 and references therein.

(4) See also: Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916–2919. Alton, E. R.; Montemayor, R. G.; Parry, R. W. *Inorg. Chem.* **1974**, *13*, 2267–2270.

(5) duMont, W. W.; Kroth, H.-J.; Schumann, H. *Chem. Ber.* **1976**, *109*, 3017–3024.

(6) Shagvaleev, F. Sh.; Zykova, T. V.; Tarasova, R. I.; Sitdikova, T. Sh.; Moskva, V. V. *Zh. Obshch. Khim.* **1990**, *60*, 1775–1779.

(7) General procedures: All reactions were performed in evacuated vessels (Burford, N.; Muller, J.; Parks, T. M. *J. Chem. Educ.*, in press). $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on samples sealed in evacuated glass using a Bruker AC-250 (250.13 MHz for ^1H, 62.89 MHz for ^{13}C, 101.26 MHz for ^{31}P). All solution chemical shifts are reported at room temperature in ppm relative to external standards, 85% H_3PO_4 for ^{31}P and TMS for ^1H and ^{13}C. Solid-state ^{31}P CP-MAS NMR spectra were obtained on a Bruker AMX-400 (400.13 MHz for ^1H, 161.98 MHz for ^{31}P) and are referenced to solid $NH_4H_2PO_4$ which has a chemical shift of +0.81 ppm relative to 85% H_3PO_4. Each CP-MAS NMR experiment was carried out at several sample spinning frequencies from 4.0 to 10.0 kHz. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer.

(8) NMR solution studies of reaction mixtures (1 mL of CD_2Cl_2): (a) Me_2PCl (0.7 mmol) and $GaCl_3$ (0.68 mmol), $^{31}P\{^1H\}$, 96 ppm (d, $^1J_{PP}$ = 311 Hz), 57 ppm (s, <5%), −28 ppm (d, $^1J_{PP}$ = 311 Hz), ^1H, 2.59 ppm (d of d, $^2J_{PH}$ = 11.3 Hz, $^3J_{PH}$ = 4.7 Hz, 6H), 1.75 ppm (d of d, $^2J_{PH}$ = 22.7 Hz, $^3J_{PH}$ = 2.1 Hz, 6H); (b) Me_2PCl (0.7 mmol) and $GaCl_3$ (1.5 mmol), $^{31}P\{^1H\}$, 89 ppm (d, $^1J_{PP}$ = 219 Hz), 56 ppm (s, <5%), −16 ppm (d, $^1J_{PP}$ = 219 Hz), ^1H (major signals >95%), 2.90 ppm (d of d, $^2J_{PH}$ = 11.6 Hz, $^3J_{PH}$ = 5.0 Hz), 2.15 ppm (d of d, $^2J_{PH}$ = 17.5 Hz, $^3J_{PH}$ = 6.3 Hz); (c) Me_2PCl (1.1 mmol) and $GaCl_3$ (0.53 mmol), $^{31}P\{^1H\}$, 99 ppm (d, $^1J_{PP}$ = 340 Hz), 57 ppm (s, <5%), −33 ppm (d, $^1J_{PP}$ = 340 Hz), ^1H (major signals >95%), 2.50 ppm (d of d, $^2J_{PH}$ = 11.1 Hz, $^3J_{PH}$ = 4.4 Hz, 6H), 1.53 ppm (d of d, $^2J_{PH}$ = 24.2 Hz, $^3J_{PH}$ = 4.6 Hz, 6H).

(9) **3**[$GaCl_4$]: Me_2PCl (5.8 mmol) in CH_2Cl_2 (10 mL) was added to $GaCl_3$ (5.8 mmol) in CH_2Cl_2 (10 mL). Removal of solvent *in vacuo* gave a white crystalline solid (crude yield 96%), which was recrystallized from n-C_6H_{14} (5 mL) and C_6H_6 (10 mL) (yield 33%); moisture sensitive. Anal. Calcd: H, 2.22; C, 8.81. Found: H, 2.17; C, 8.69. NMR (CD_2Cl_2): $^{31}P\{^1H\}$, 98 ppm (d, $^1J_{PP}$ = 332 Hz), 57 ppm (s, <5%), −31 ppm (d, $^1J_{PP}$ = 332 Hz); ^1H, 2.54 ppm (d of d, $^2J_{PH}$ = 11.0 Hz, $^3J_{PH}$ = 4.6 Hz, 6H), 1.69 ppm (d of d, $^2J_{PH}$ = 23.9 Hz, $^3J_{PH}$ = 4.0 Hz, 6H); $^{13}C\{^1H\}$, 16.5 ppm (d of d, $^1J_{PC}$ = 39.1 Hz, $^2J_{PC}$ = 5.7 Hz), 7.4 ppm (d of d, $^1J_{PC}$ = 18.6 Hz, $^2J_{PC}$ = 4.3 Hz). Solid-state $^{31}P\{^1H\}$ CP-MAS NMR: 84 ppm (d, $^1J_{PP}$ = 154 Hz), −16 ppm (broad). IR: 1297 (s), 1167 (w), 1156 (w), 955 (s), 931 (m), 922 (m), 903 (s), 892 (s), 868 (w), 837 (w), 777 (w), 757 (w), 688 (w), 573 (s), 461 (w), 411 (s), 367 (s) cm^{-1}. Mp: 78–81 °C.

(10) Crystal data for **3**[$GaCl_4$]: $C_4H_{12}Cl_8Ga_2P_2$, M = 545.15, monoclinic, $P2_1/c$, a = 10.227(2) Å, b = 13.504(3) Å, c = 13.968(4) Å, β = 91.39(2)°, V = 1928(1) Å^3, Z = 4, D_{calcd} = 1.878 Mg m^{-3}, μ = 40.40 cm^{-1}. Data (2828 unique reflections) were collected at 23 ± 1 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) using the $\omega - 2\theta$ scan technique ($2\theta_{max}$ = 46°). The structure was solved by direct methods and refined by full-matrix least-squares refinement of F^2 to R = 0.0887, R_w = 0.1107, GOF = 3.93 for 2681 reflections with $I > 2\sigma(I)$ (161 parameters and 14 restraints). The cation is disordered, and all atoms except C1 and C3 occupy two positions which were located from a Fourier difference map. All atoms except C2 and C4 were refined anisotropically. The geometry of this part of the molecule was restrained so that chemically equivalent bonds are approximately equal. The empirical correction for absorption using DIFABS was applied. All calculations were performed using SHELX-93, Sheldrick, G. M., unpublished.

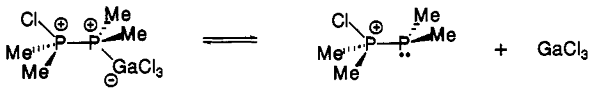
(11) A similar complex was speculated on the basis of ^{31}P NMR data: Schmidpeter, A.; Lochschmidt, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 253–254. Lochschmidt, S.; Muller, G.; Huber, B.; Schmidpeter, A. *Z. Naturforsch.* **1986**, *41b*, 444–454.

(12) Schomburg, D.; Bettermann, G.; Ernst, L.; Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 975–976. See also, for $Me_2P(S)P(S)Me_2$, P–P = 2.245(6) Å: Lee, J. D.; Goodacre, G. W. *Acta Crystallogr.* **1971**, *B27*, 302–307. For $Me_2P(BH_3)P(BH_3)Me_2$, P–P = 2.189(5) Å: Carrell, H. L.; Donohue, J. *Acta Crystallogr.* **1968**, *B24*, 699–707.

0002-7863/94/1516-6474$04.50/0

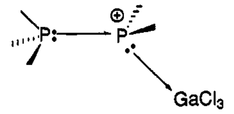
–31 ppm, ${}^1J_{PP}$ = 332 Hz) or an equimolar reaction mixture. Moreover, solid obtained[13] from the $2Me_2PCl/GaCl_3$ solution has a substantially higher melting point than **3**[$GaCl_4$] and exhibits solid-state isotropic chemical shifts and a coupling constant ($\delta_{isotropic}$ = 99 ppm, –36 ppm, ${}^1J_{PP}$ = 331 Hz) consistent with those observed in the $2Me_2PCl/GaCl_3$ solution. All spectra contain a singlet at 57 ppm of less than 5% relative intensity, assigned to $Me_2(Cl)P \rightarrow GaCl_3$, which is possibly in equilibrium with the diphosphorus cations.

These spectroscopic observations demonstrate a facile dissociation of the new cation **3** in solution to give cation **4**, as seen in equimolar reaction mixtures of Me_2PCl and $GaCl_3$ and those containing limited amounts of $GaCl_3$. When excess $GaCl_3$ is present, the equilibrium favors **3**. The low-frequency signal (–36 ppm) in the solid-state ${}^{31}P$ NMR spectrum of **4**[$GaCl_4$] is a sharp doublet, while the corresponding signal (–16 ppm) for **3**[$GaCl_4$] is broadened by interaction with the quadrupolar gallium nucleus.


3 **4**

Although a number of coordination complexes involving Lewis acidic phosphenium centers have been identified by solution NMR spectroscopy,[4,6] infrared spectroscopy, and conductivity measurements,[1,14] only two structural characterizations have been reported recently.[15,16] Our observations provide rare structural confirmation of the P–P coordinative bond in phosphinophosphonium[6] cations, but more importantly illustrate the weak Lewis basicity of the cation **4** toward $GaCl_3$ to give **3**. A somewhat related nickel complex has been speculated as an intermediate in the formation of $[(PPh_3)_3Ni{=}P{=}C(SiMe_3)_2][AlCl_4]$, although characterization data is not presented.[16]

Reaction of aminophosphinophosphonium cations with excess Lewis acid results in quantitative formation of the corresponding aminophosphenium cations **2**,[14] due to the stabilization afforded by π-donation to P. The absence of such stabilization for Me_2P^+ renders the salt of chlorotetramethylphosphinophosphonium–gallium trichloride complex thermodynamically favored with respect to 2 equiv of the ionic $[Me_2P][GaCl_4]$. Comprehensive characterization of **3**[$GaCl_4$] here portrays and example of "*in series*" **5** coordination, a phosphine base (Me_2PCl) coordinated to a Lewis acidic phosphenium cation (Me_2P^+) induces a coordination to $GaCl_3$. We anticipate the discovery of other complexes involving these linkages, possibly leading to oligomeric or polymeric systems.


5

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council of Canada. We thank the Atlantic Region Magnetic Resonance Centre for use of instrumentation and Professor Rod Wasylishen for helpful comments.

Supplementary Material Available: X-ray crystallographic data for $[P(GaCl_3)Me_2P(Cl)Me_2][GaCl_4]$ {**3**[$GaCl_4$]}, including crystal data, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles (4 pages); listing of observed and calculated structure factors for **3**[$GaCl_4$] (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(13) **4**[$GaCl_4$]: Me_2PCl (3.4 mmol) in CH_2Cl_2 (10 mL) was added to $GaCl_3$ (1.7 mmol) in CH_2Cl_2 (5 mL). Removal of solvent *in vacuo* gave a white crystalline solid (crude yield 84%), moisture sensitive. NMR (CD_2Cl_2): ${}^{31}P\{{}^1H\}$, 99 ppm (d, ${}^1J_{PP}$ = 340 Hz), –32 ppm (d, ${}^1J_{PP}$ = 341 Hz), 57 ppm (s, <5%); ${}^1H$ (major signals >95%), 2.55 ppm (d of d, ${}^2J_{PH}$ = 11.3 Hz, ${}^3J_{PH}$ = 4.4 Hz, 6H), 1.65 ppm (d of d, ${}^2J_{PH}$ = 24.3 Hz, ${}^3J_{PH}$ = 4.9 Hz, 6H); ${}^{13}C\{{}^1H\}$, 16.5 ppm (d of d, ${}^1J_{PC}$ = 38.2 Hz, ${}^2J_{PC}$ = 5.7 Hz), 7.7 ppm (d of d, ${}^1J_{PC}$ = 21.0 Hz, ${}^2J_{PC}$ = 4.8 Hz). Solid-state ${}^{31}P\{{}^1H\}$ CP-MAS NMR: 99 ppm (d, ${}^1J_{PP}$ = 331 Hz), 57 ppm (s, <10%), –36 ppm (d, ${}^1J_{PP}$ = 331 Hz). IR: 1410 (s), 1297 (s), 1169 (w), 1151 (w), 1104 (w), 960 (s), 929 (s), 888 (s, sh), 835 (w), 777 (m), 662 (w), 550 (s), 500 (w), 426 (m), 368 (s), 309 (w) cm^{-1}. Mp: 236–246 °C.

(14) Shultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046–3050. Thomas, M. G.; Shultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994–1001.

(15) Reed, R.; Reau, R.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 399–401.

(16) David, G.; Niecke, E.; Nieger, M.; Radseek, J.; Schoeller, W. W. *J. Am. Chem. Soc.* **1994**, *116*, 2191–2192.