A Crystalline Phosphenium Salt Featuring the Electron-Withdrawing 2,6-Bis(trifluoromethyl)phenyl Group

Anca Dumitrescu,[a] Heinz Gornitzka,[a] Wolfgang W. Schoeller,[b] Didier Bourissou,[a] and Guy Bertrand*[a,c]

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The presence of a σ-withdrawing group such as the 2,6-bis-(trifluoromethyl)phenyl substituent does not prevent the isolation of a highly electrophilic phosphenium salt.

Introduction

Bulky hydrocarbon substituents are commonly used for the thermodynamic and kinetic stabilization of highly reactive species such as low-coordinate compounds.[1] Due to their peculiar properties,[2] related fluorinated substituents have recently attracted considerable attention, and have allowed for the isolation of several group 14 carbenoids (Figure 1). The stability of the monomeric bis(aryl)germylene,[3] -stannylene[4] and -plumbylene[5] **I**−**III** is only partly due to steric shielding,[6] the most important factor being the electron-donating ability of the fluorine lone pairs of the *o*-CF_3 groups to the electron-deficient center. Carbenes are even more reactive,[7] but using their reluctance to insert into C−F compared to C−H bonds,[8] the highly persistent triplet bis(aryl)carbene **IV**[9] and the first stable singlet (aryl)carbenes **V**[10] and **VI**[11] have been prepared. The 2,6-bis(trifluoromethyl)phenyl group Ar_F remains electronically a spectator in the (amino)(aryl)carbenes **V**,[10] while its electron-withdrawing properties are involved in the push-pull stabilization of the (aryl)(phosphanyl)carbenes **VI**.[11]

Much less is known about the group 15 carbenoids.[12] Because of their inherent electrophilicity, most of the known phosphenium salts (R_2P^+) feature two π-donor substituents such as amino groups.[13] Notable exceptions are the (amino)(mesityl)-[14] and (phosphanyl)(supermesityl)-phosphenium[15] salts, which both feature an electron-rich

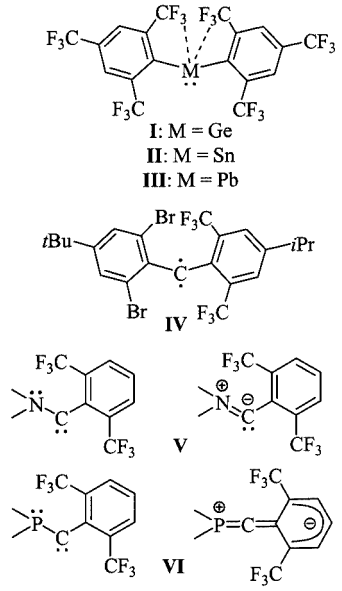


Figure 1. Structure of group 14 carbenoids **I**−**VI**

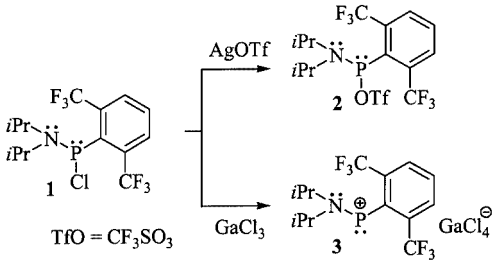
aryl substituent. Given the potential uses of phosphenium salts as strong π-acceptor ligands,[16] it was of interest to investigate the possibility of preparing a phosphenium salt featuring an electron-withdrawing group. Here we report the synthesis, structural analysis and reactivity of the [2,6-bis(trifluoromethyl)phenyl](diisopropylamino) phosphenium salt **3**.

Results and Discussion

Treatment of the chlorophosphane **1** with silver trifluoromethanesulfonate in dichloromethane, a common method for preparing phosphenium salts, led to derivative **2** (Scheme 1), which was isolated as white crystals in 70% yield. The covalent nature of **2** was suggested by the mod-

[a] Laboratoire d'Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069)
Université Paul Sabatier
118, route de Narbonne, 31062 Toulouse Cedex 04, France
Fax: (internat.) +33-5/6155-8204
[b] Fakultät für Chemie der Universität
Postfach 10 01 31, 33615 Bielefeld, Germany
Fax: (internat.) +49-(0)521/106-6467
[c] UCR-CNRS Joint Research Chemistry Laboratory (UMR 2282), Department of Chemistry − University of California, Riverside, CA 92521−0403, USA
Fax: (internat.) +1-909/787-2725
E-mail: gbertran@mail.ucr.edu

erate deshielding of the ^{31}P NMR signal (**1**: δ = 123.9 ppm; **2**: δ = 186.5 ppm), and confirmed by an X-ray analysis (Figure 2 and Table 1). Compound **2** is the first covalent (trifluoromethanesulfonate)phosphane to be structurally characterized.[17] The P(1)−N(1) bond is very short [1.626(4) Å] and the P(1)−O(1) bond is very long [1.882(2) Å], suggesting that a less coordinating anion should allow for the isolation of the highly electrophilic ionic form. Indeed, the desired phosphenium salt **3** was obtained from **1** by chloride abstraction with gallium trichloride (Scheme 1). The ionic nature of **3** in solution was unambiguously deduced from the dramatic downfield shift observed in the ^{31}P NMR spectrum (**3**: δ = 423 ppm). Single crystals of **3** suitable for an X-ray analysis were obtained from dichloromethane solution at low temperature (Figure 3 and Table 1).



Scheme 1. Synthesis of compounds **2** and **3**

The values of the shortest P···Cl contacts [3.378(9) and 3.848(6) Å] confirm the ionic nature of **3**. The nitrogen atom is in a planar environment and the P(1)−N(1) bond is short

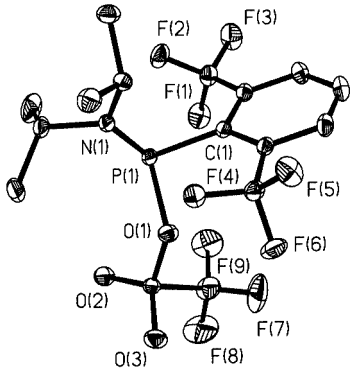


Figure 2. Thermal ellipsoid diagram (30% probability) of **2**; the hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and angles (°): P(1)−N(1) 1.626(4), P(1)−C(1) 1.863(3), P(1)−O(1) 1.882(2), N(1)−P(1)−C(1) 104.15(10), N(1)−P(1)−O(1) 110.03(9), C(1)−P(1)−O(1) 91.38(12), C(9)−N(1)−C(12) 114.96(18), C(9)−N(1)−P(1) 129.06(11), C(12)−N(1)−P(1) 115.81(12)

[1.605(2) Å], as expected from the donation of the nitrogen lone pair to the vacant 3p(P) orbital. The aryl group is almost perpendicular to the plane defined by the C(9), C(12), N(1), P(1) and C(1) atoms [torsion angle N(1)−P(1)−C(1)−C(2) 94.8(2)°], which rules out any conjugation of the π system with the vacant 3p(P) orbital. Of further interest, the absence of an interaction between the phosphorus lone pair and the withdrawing aryl group is confirmed by the small C(1)−P(1)−N(1) angle [105.1(1)°] and the long P(1)−C(1) bond [1.845(2) Å]. All these data suggest that there is no π interaction between the aryl group and the phosphorus center, as observed for the (amino)(aryl)carbene

Table 1. Crystallographic data for compounds **2**, **3** and **5b**

	2	**3**	**5b**
Empirical formula	$C_{15}H_{17}F_9NO_3PS$	$C_{14}H_{17}Cl_4F_6GaNP$	$C_{33}H_{57}Cl_4F_6GaN_5P$
M_r	493.33	555.78	880.33
Crystal size [mm]	0.1 × 0.5 × 0.7	0.2 × 0.5 × 0.8	0.1 × 0.4 × 0.6
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a [Å]	8.83(2)	9.2399(3)	13.7512(11)
b [Å]	15.74(3)	10.2700(4)	16.9623(13)
c [Å]	14.63(2)	13.7886(5)	18.4099(14)
α [°]	90	73.0520(10)	90
β [°]	92.48(9)	88.8350(10)	90
γ [°]	90	65.6620(10)	90
V [Å^3]	2032(7)	1132.89(7)	4294.1(6)
Z	4	2	4
D_x [Mg m^{-3}]	1.613	1.629	1.362
μ [mm^{-1}]	0.336	1.805	0.982
F(000)	1000	552	1832
T [K]	193(2)	193(2)	193(2)
$2\theta_{max}$ [°]	65	56	50
No. of refl. measured	24985	11644	38281
No. of refl. unique	6890	5583	7235
R_{int}	0.0526	0.0176	0.0578
Parameters	275	322	465
Restraints	0	166	0
wR_2 (all reflns.)	0.1119	0.0835	0.0871
R_1 [$I > 2\sigma I$]	0.0383	0.0316	0.0406
Max. Δρ (e·Å^{-3}]	0.414	0.459	0.430

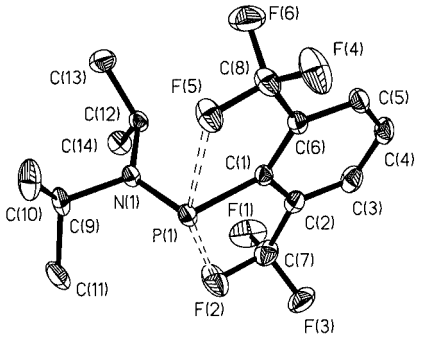


Figure 3. Thermal ellipsoid diagram (30% probability) of **3**; the hydrogen atoms and $GaCl_4^-$ counteranion have been omitted for clarity; selected bond lengths (Å) and angles (°): P(1)−N(1) 1.6050(15), P(1)−C(1) 1.8454 (18), C(1)−C(2) 1.404(3), N(1)−P(1)−C(1) 105.08(8)

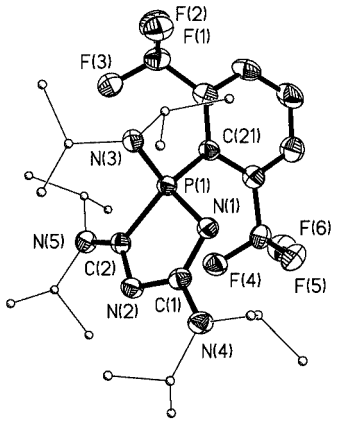
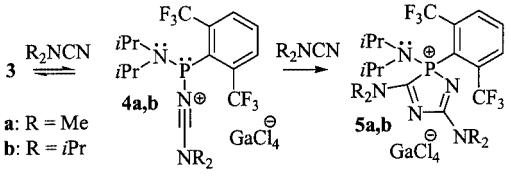


Figure 4. Thermal ellipsoid diagram (50% probability) of **5b**; for clarity the isopropyl groups have been simplified, and the hydrogen atoms and $GaCl_4^-$ counteranion omitted; selected bond lengths (Å) and angles (°): P(1)−N(3) 1.642(3), P(1)−C(21) 1.850(3), P(1)−C(2) 1.884(3), P(1)−N(1) 1.605(3), N(3)−P(1)−C(21) 112.25(15)

V. However, two close P···F contacts are present in the solid state [2.554(2) and 2.562(11) Å, sum of the van der Waals radii: 3.37 Å], as observed for the heavier group 14 carbenoids. Low-temperature experiments were prevented by the poor solubility of **3**, but the presence of a single ^{19}F NMR signal at room temperature suggests fast rotation of the *o*-CF_3 groups and thus weak P···F interactions.

The high electrophilicity of **3** is apparent from its chemical behavior. Cyanamides do not react with the bis(diisopropylamino)phosphenium salt. In marked contrast, however, dimethylcyanamide reacts smoothly with **3** (Scheme 2) The cationic five-membered heterocycle **5a** was obtained in 60% yield and characterized by multinuclear NMR spectroscopy. The formation of **5a** probably results from a [3+2] dipolar cycloaddition between the acid-base complex **4a** and a second molecule of cyanamide. This hypothesis was confirmed using diisopropylcyanamide. Steric protection allowed the characterization of the acid-base adduct **4b** when only one equivalent of cyanamide was used (Scheme 2). Addition of a second equivalent led to the cationic five-membered heterocycle **5b**, which was isolated in 65% yield as white crystals and structurally characterized (Figure 4 and Table 1).



Scheme 2. Synthesis of compounds **4** and **5**

Concluding Remarks

The presence of an electron-withdrawing group such as a 2,6-bis(trifluoromethyl)-substituted aryl does not prevent the isolation of highly electrophilic phosphenium salts **3**. According to X-ray analysis, its structure is half-way between that of the related carbenes and heavier homologues. The electrophilic character of **3** is illustrated by the unusual formation of acid-base complexes **4** with cyanamides. The availability of phosphenium salts featuring a withdrawing group opens the way for new developments in the coordination chemistry of strong π-acceptor ligands.

Experimental Section

General Procedures: All reactions and manipulations were carried out under dry nitrogen in conventional glassware using standard Schlenk techniques. Solvents were dried according to standard procedures. ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker AC200, WM250 or AMX400 spectrometers. All downfield chemical shifts are expressed with a positive sign, in ppm, relative to an external standard (Me_4Si for ^1H and ^{13}C, CF_3CO_2H for ^{19}F and 85% H_3PO_4 for ^{31}P).

Synthesis of the Chlorophosphane 1: Diisopropylamine (2 g, 19 mmol) was added to a toluene solution (15 mL) of 2,6-bis(trifluoromethyl)phenyldichlorophosphane (3 g, 9.5 mmol) and the reaction mixture was refluxed for 18 h. The solvent was then removed under vacuum and the residue extracted with pentane (30 mL). The chlorophosphane **1** was crystallized from a pentane solution at −30 °C. Yield 2.7 g (75%); m.p. 94 °C. ^1H NMR (CD_2Cl_2): δ = 1.1 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 1.3 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 3.6 (sept, $^3J_{H,H}$ = 6.7 Hz, 2 H, C*H*CH_3), 7.7 (t, $^3J_{H,H}$ = 8.2 Hz, 1 H, H_p), 8.0 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_m) ppm. ^{19}F NMR (CD_2Cl_2): δ = 22.4 (d, $^4J_{P,F}$ = 44 Hz) ppm. ^{31}P NMR (CD_2Cl_2): δ = 123.9 (sept, $^4J_{P,F}$ = 44 Hz) ppm. $C_{14}H_{17}ClF_9NP$ (436.7): calcd. C 38.50, H 3.92, N 3.21; found C 38.78, H 4.23, N 2.99.

Synthesis of the (Trifluoromethylsulfonyl)phosphane (2): Silver trifluoromethanesulfonate (2.1 g, 7.9 mmol) was added to a dichloromethane solution (15 mL) of the chlorophosphane **1** (3 g, 7.9 mmol) at −78 °C. After warming to room temperature and filtration, the phosphane **2** was crystallized from a dichloromethane solution at −30 °C. Yield 2.7 g (70%). ^1H NMR ($CDCl_3$): δ = 0.9 (d, $^3J_{H,H}$ = 5.4 Hz, 6 H, CH_3), 1.3 (d, $^3J_{H,H}$ = 5.4 Hz, 6 H, CH_3), 3.3 (sept, $^3J_{H,H}$ = 5.4 Hz, 1 H, C*H*CH_3), 3.4 (sept, $^3J_{H,H}$ = 5.4 Hz, 1 H, C*H*CH_3), 6.7 (t, $^3J_{H,H}$ = 6.4 Hz, 1 H, H_p), 7.4 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, H_m) ppm. ^{19}F NMR ($CDCl_3$): δ = 12.7 (s, 3 F, CF_3SO_3), 20.3 (d, $^4J_{P,F}$ = 43 Hz, 6 F, *o*-CF_3) ppm. ^{31}P NMR

($CDCl_3$): δ = 186.5 (sept, $^4J_{P,F}$ = 43 Hz) ppm. $C_{15}H_{17}F_9NO_3PS$ (493.3): calcd. C 36.52, H 3.47, N 2.84; found C 36.15, H 3.26, N 3.14.

Synthesis of the Phosphenium Salt 3: Gallium trichloride (0.46 g, 2.6 mmol) was added to a dichloromethane solution (4 mL) of the chlorophosphane **1** (1 g, 2.6 mmol) at −78 °C. After warming to room temperature, the reaction mixture was stirred for 30 minutes. The phosphenium salt **3** was crystallized from a dichloromethane solution at −30 °C. Yield 0.9 g (62%); m.p. 164 °C. ^{1}H NMR (CD_2Cl_2): δ = 1.6 (br., 12 H, CH_3), 4.4 (br., 2 H, C*H*CH_3), 8.3 (br., 3 H, H_p and H_m) ppm. ^{13}C NMR (CD_2Cl_2): δ = 25.0 (br., CH3), 62.7 (br., CHCH3), 124.3 (q, $^1J_{C,F}$ = 276 Hz, CF_3), 128.5 (d, $^1J_{C,P}$ = 78 Hz, C_{ipso}), 133.4 (s, C_m), 133.3 (q, $^2J_{C,F}$ = 32 Hz, C_o), 136.5 (s, C_p) ppm. ^{19}F NMR (CD_2Cl_2): δ = 22.4 (d, $^4J_{P,F}$ = 40 Hz) ppm. ^{31}P NMR (CD_2Cl_2): δ = 423 (br.) ppm. $C_{14}H_{17}Cl_4F_6GaNP$ (555.8): calcd. C 30.25, H 3.08, N 2.52; found C 29.87, H 2.78, N 2.35.

Synthesis of the Heterocycle 5a: Dimethylcyanamide (0.05 g, 0.68 mmol) was added at room temperature to a dichloromethane solution (4 mL) of the phosphenium salt **3** (0.2 g, 0.34 mmol). The reaction mixture was stirred for 30 minutes and the solvent was evaporated under vacuum. The heterocycle **5a** was crystallized from a 1:2 dichloromethane/diethyl ether solution at −30 °C. Yield 0.18 g (60%). ^{1}H NMR (CD_2Cl_2): δ = 1.4 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CHC*H*$_3$), 1.5 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CHC*H*$_3$), 3.2 (d, $J_{P,H}$ = 1.2 Hz, 3 H, NCH_3), 3.2 (s, 3 H, NCH_3), 3.3 (d, $J_{P,H}$ = 0.8 Hz, 3 H, NCH_3), 3.6 (b, 3 H, NCH_3), 3.8 (sept.d, $^3J_{H,H}$ = 6.4, $^3J_{P,H}$ = 19.2 Hz, 2 H, C*H*CH_3), 8.1 (pseudo-t, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_p), 8.2 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_m), 8.3 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_m) ppm. ^{13}C NMR (CD_2Cl_2): δ = 22.0 (s, CH*C*H$_3$), 22.9 (s, CH*C*H$_3$), 37.7 (d, $J_{C,P}$ = 3.6 Hz, NCH_3), 38.2 (s, NCH_3), 43.5 (s, NCH_3), 43.6 (s, NCH_3), 52.6 (s, *C*HCH$_3$), 123.5 (q, $^1J_{C,F}$ = 275 Hz, CF_3), 126.2 (d, $^1J_{C,P}$ = 108 Hz, C_{ipso}), 133.0 (q, $^2J_{C,F}$ = 32 Hz, C_o), 133.1 (q, $^2J_{C,F}$ = 33 Hz, C_o), 133.6 (s, C_m), 133.7 (s, C_m), 135.2 (s, C_p), 166.3 (d, $J_{P,C}$ = 24 Hz, CN), 175.2 (d, $J_{P,C}$ = 37 Hz, CN) ppm. ^{31}P NMR (CD_2Cl_2): δ = 64.2 (s) ppm. $C_{26}H_{29}Cl_4F_6GaN_5P$ (768.0): calcd. C 40.66, H 3.81, N 9.12; found C 40.31, H 3.42, N 9.54.

Synthesis of the Acid-Base Adduct 4b: Diisopropylcyanamide (0.04 g, 0.34 mmol) was added at room temperature to a dichloromethane solution (4 mL) of the phosphenium salt **3** (0.2 g, 0.34 mmol). The reaction was stirred for 1 h and the solvent was evaporated under vacuum. The acid-base adduct **4b** was obtained as a colorless oil and characterized without purification. Yield 0.14 g (60%). ^{1}H NMR (CD_2Cl_2): δ = 1.1 (d, $^3J_{H,H}$ = 5.6 Hz, 6 H, CHC*H*$_3$), 1.4 (d, $^3J_{H,H}$ = 6.5 Hz, 12 H, CHC*H*$_3$), 1.5 (d, $^3J_{H,H}$ = 5.6 Hz, 6 H, CHC*H*$_3$), 3.6 (br., 1 H, C*H*CH$_3$), 3.8 (br., 2 H, C*H*CH$_3$), 3.9 (br., 1 H, C*H*CH$_3$), 8.0 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, H_p), 8.2 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, H_m) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.4 (s, CH*C*H$_3$), 22.0 (s, CH*C*H$_3$), 26.0 (d, $J_{C,P}$ = 8 Hz, CH*C*H$_3$), 49.0 (d, $J_{C,P}$ = 24 Hz, *C*HCH$_3$), 56.1 (s, *C*HCH$_3$), 56.8 (s, *C*HCH$_3$), 124.0 (q, $^1J_{C,F}$ = 276 Hz, *o*-CF_3), 129.0 (d, $^1J_{C,P}$ = 48 Hz, C_{ipso}), 132.9 (q, $^3J_{C,F}$ = 32 Hz, C_m), 134.0 (s, C_p), 134.5 (dq, $J_{C,P}$ = 17, $^2J_{C,F}$ = 30 Hz, C_o) ppm. ^{31}P NMR (CD_2Cl_2): δ = 110.9 (br.) ppm.

Synthesis of the Heterocycle 5b: Diisopropylcyanamide (0.08 g, 0.68 mmol) was added at room temperature to a dichloromethane solution (4 mL) of the phosphenium salt **3** (0.2 g, 0.34 mmol). The reaction was stirred for 2 h and the solvent was evaporated under vacuum. The heterocycle **5b** was crystallized from a 1:2 dichloromethane/diethyl ether solution at −30 °C. Yield 0.22 g (65%). ^{19}F NMR ($CDCl_3$): δ = 22.7 (s) ppm. ^{31}P NMR ($CDCl_3$): δ = 57.1 (s) ppm. $C_{28}H_{45}Cl_4F_6GaN_5P$ (808.2): calcd. C 41.61, H 5.61, N 8.67; found C 41.99, H 5.87, N 8.44.

X-ray Crystallographic Studies of Compounds 2, 3 and 5b: Crystal data for all structures are presented in Table 1. Data were collected on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods by means of SHELXS-97[18] and refined with all data on F^2 by means of SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model.
CCDC-179375 (**2**), -179376 (**3**) and -179377 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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