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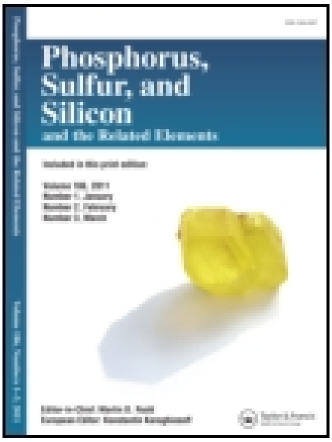

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New Monocationic Trialkylphosphine Tetraphenylborate Salts

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NEW MONOCATIONIC TRIALKYLPHOSPHINE TETRAPHENYLBORATE SALTS

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Abstract *Six new monocationic trialkylphosphines, $[P(CH_2NH_2R)\{CH_2N(R)CH_2N(R)CH_2\}]^+$ ($R = C_6H_5CH_2$, $4\text{-}FC_6H_4CH_2$, $4\text{-}ClC_6H_4CH_2$, $4\text{-}CH_3C_6H_4CH_2$) as their Cl^- (**1c**, **1d**) or BPh_4^- (**2a**–**2d**) salts, are described. All compounds have been characterized by $^{31}P\{^1H\}$ spectroscopy, FTIR spectroscopy, and elemental analysis. A single crystal X-ray structure determination of **2a** has been performed. In contrast to recent examples reported by us, only one intramolecular N–H···N hydrogen bond was observed in molecules of **2a**; the other N–H was involved in an N–H···π intermolecular interaction to the BPh_4^- anion.*

Keywords Anion metathesis; ligands; spectroscopy; tertiary phosphine; X-ray crystallography

INTRODUCTION

Water-soluble tertiary phosphines are widely recognized as an important class of ligand finding uses in coordination chemistry and catalysis. One noteworthy example is 1,3,5-triaza-7-phosphaadamantane (PTA),[1] which has received much recent interest for its ease of chemical modification,[2,3] diverse metal coordination,[4] and cytotoxic[5,6] and catalytic properties.[7,8] As part of continuing studies investigating new horizons in phosphine chemistry, we recently prepared the charged variants **1a/1b** (Scheme 1), which are structurally related to PTA. Moreover we showed that the diamondoid framework in **1a/1b** is conformationally locked, in the solid state, through two intramolecular N–H···N hydrogen bonds using the quaternary dialkylammonium/tertiary nitrogen atoms as donor/acceptor sites, respectively.[9] This structural motif remains unaltered, even after complexation to Ru^{II} or Rh^{III} metal centers. The behavior of these ligands towards Pd^{II} or Pt^{II} metal centers was also illustrated by the formation of unusual homodinuclear zwitterionic complexes containing a partially delocalized $P\{cyclo\text{-}CH_2N(R)CHN(R)CH_2\}$ bridging phosphido ligand.[10] In this article, we describe the synthesis and characterization of two further derivatives of **1** and also a series of tetraphenylborate salts **2a**–**2d**. The single crystal X-ray structure determination of **2a** revealed a new structural motif to that previously observed for **1a/1b** and its related analogues.[9]

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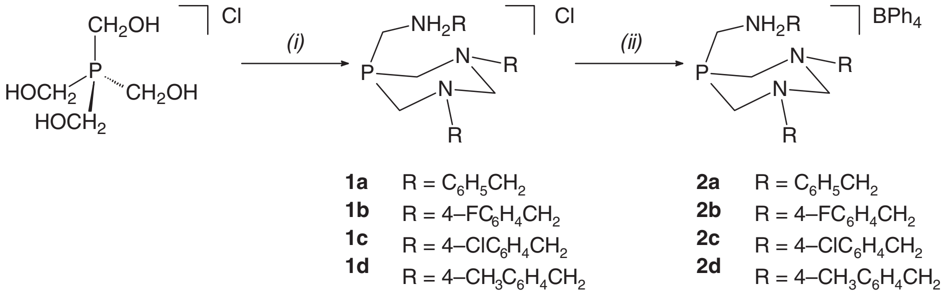

Scheme 1 (i) ~4 equiv. 4-$XC_6H_4CH_2NH_2$ (X = Cl or CH_3), EtOH, r.t. (ii) 1.5 equiv. Na[BPh_4], MeOH.

RESULTS AND DISCUSSION

The monocationic chloride salts **1c** (R = 4-$ClC_6H_4CH_2$) and **1d** (R = 4-$CH_3C_6H_4CH_2$) were synthesized from commercially available [$P(CH_2OH)_4$]Cl (THPC) and approx. 4 equiv. of 4-$XC_6H_4CH_2NH_2$ (X = Cl, CH_3) according to a previously published procedure (Scheme 1).[9] Facile anion metathesis of **1a**−**d** with Na[BPh_4] in MeOH afforded the corresponding tetraphenylborate salts **2a**−**d** in excellent yields (around 90%). In all four cases, the $^{31}P\{^1H\}$ NMR spectra revealed a predominant species around δ(P) −55 ppm [recorded in $(CD_3)_2SO$]. All compounds were further characterized by FT−IR spectroscopy, FAB−MS, and elemental analysis (see the Experimental section for selected data).

Suitable crystals of **2a** were obtained by vapor diffusion of diethyl ether into a CH_2Cl_2 solution over the course of several days. The single crystal X-ray structure[11] of **2a** has been determined (Figure 1), with selected bond lengths and angles given in Table 1. The

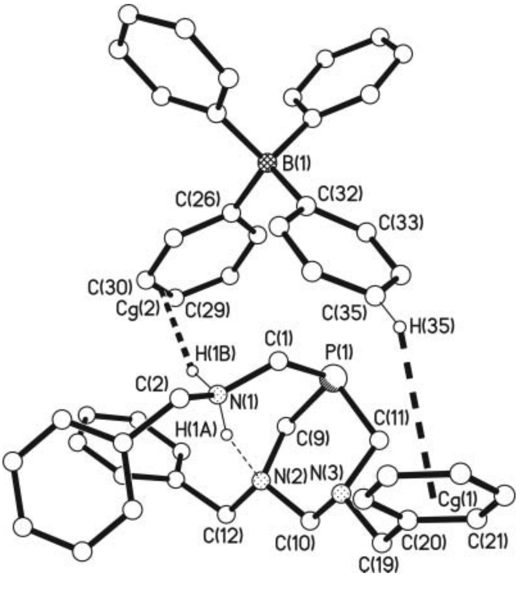

Figure 1 Crystal structure of **2a**. All hydrogen atoms except H(1A), H(1B), and H(35) have been omitted for clarity. Cg(1) is the centroid of the phenyl group C(20) to C(25); Cg(2) is the midpoint between atoms C(29) and C(30).

Table 1 Selected bond lengths (Å) and angles (°) for **2a**

P(1)–C(1)	1.8581(16)	C(11)–N(3)	1.4664(17)
P(1)–C(9)	1.8457(13)	C(1)–P(1)–C(9)	100.54(6)
P(1)–C(11)	1.8407(14)	C(1)–P(1)–C(11)	98.39(7)
C(1)–N(1)	1.4816(19)	C(9)–P(1)–C(11)	97.38(6)
C(9)–N(2)	1.4772(17)		

phosphorus environment in **2a** is best described as pyramidal, and the P—C—N—C—N—C six-membered ring adopts the expected chair conformation. The P–C and P–N bond distances are broadly as expected and in keeping with values previously reported in the literature.[9] The most striking feature of **2a** is the presence of a single intramolecular N(1)–H(1A)···N(2) hydrogen bond [N(1)···N(2) 2.7393(17) Å, H(1A)···N(2) 1.887(18) Å; N(1)–H(1A)···N(2) 148.4(16)°] unlike the two intramolecular N–H···N contacts found in **1b** and variants (SbF_6^-, PF_6^-) thereof [N···N range 2.804(3)–2.915(5) Å].[9] There are also N(1)–H(1B)···π {Cg(2)} (2.42 Å) and C(35)–H(35)···π {Cg(1)} (3.38 Å) interactions between the cation and the BPh_4^- anion.

In summary, we have shown that new monocationic trialkylphosphines, as their tetraphenylborate salts, can be readily prepared. Further studies are currently underway that are looking at their coordination and organometallic chemistry.

EXPERIMENTAL

Ligands **1c** and **1d** were prepared following a previously published procedure.[9] The following method was used for the synthesis of the tetraphenylborate compound **2a**. To a solution of **1a** (0.20 g, 0.45 mmol) in HPLC grade MeOH (10 mL), Na[BPh_4] (0.23 g, 0.67 mmol) was added in the minimum volume of HPLC grade MeOH. The solution was stirred for 30 min at r.t., and the volume was concentrated to dryness under reduced pressure. The addition of distilled water (10 mL) gave a colorless solid, which was collected by suction filtration and dried under vacuum. Yield: 0.29 g, 89%. Compounds **2b** (86%), **2c** (90%), and **2d** (90%) were each prepared in a similar manner.

Selected data for **2a**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$, 298 K]: δ(P) −55.1 ppm. FT–IR (KBr): 3163, 3053, 3027, 3001, 2983, 2848, 2779 cm^{-1} (ν_{NH}/ν_{CH}). FAB–MS: *m/z* 404 [M–BPh_4]$^+$. Calcd. for $C_{49}H_{51}BN_3P$: C, 81.30; H, 7.12; N, 5.81. Found: C, 80.85; H, 6.80; N, 5.69. Selected data for **2b**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$, 298 K]: δ(P) −54.9 ppm. FT–IR (KBr): 3120, 3055, 3039, 3000, 2985, 2930, 2830, 2792 (ν_{NH}/ν_{CH}), 1227 (ν_{CF}) cm^{-1}. FAB–MS: *m/z* 458 [M–BPh_4]$^+$. Calcd. for $C_{49}H_{48}BF_3N_3P{\cdot}H_2O$: C, 73.95; H, 6.35; N, 5.28. Found: C, 74.28; H, 6.06; N, 5.39. Selected data for **2c**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$, 298 K]: δ(P) −54.5 ppm. FT–IR (KBr): 3163, 3121, 3054, 3039, 2999, 2983, 2925, 2838, 2792 (ν_{NH}/ν_{CH}), 844, 807 (ν_{CCl}) cm^{-1}. FAB–MS: *m/z* 508 [M–BPh_4]$^+$. Calcd. for $C_{49}H_{48}BCl_3N_3P{\cdot}H_2O$: C, 69.64; H, 5.98; N, 4.97. Found: C, 69.77; H, 5.75; N, 5.04. Selected data for **2d**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$, 298 K]: δ(P) −54.6 ppm. FT–IR (KBr): 3155, 3052, 2999, 2982, 2945, 2921, 2852, 2825, 2780 cm^{-1} (ν_{NH}/ν_{CH}). FAB–MS: *m/z* 446 [M–BPh_4]$^+$. Calcd. for $C_{52}H_{57}BN_3P$: C, 81.54; H, 7.52; N, 5.49. Found: C, 81.22; H, 7.52; N, 5.53.

Crystal data for **2a**: $C_{49}H_{51}BN_3P$, $M = 723.71$; monoclinic, $P2_1/c$, $a = 12.9954(4)$, $b = 19.7592(6)$, $c = 16.6069(5)$ Å, $V = 4049.3(2)$ Å^3; $Z = 4$, ρ_{cal} 1.187 g cm^{-3}; μ(Mo-Kα) = 0.106 mm^{-1}; $\lambda = 0.71073$ Å, $T = 150(2)$ K; 48008 reflections were collected on a Bruker APEX 2 CCD diffractometer[11] using narrow ω-scans, 12372 of which were independent ($R_{\text{int}} = 0.0427$). The structure was solved by Patterson synthesis and refined on F^2 values to give a final $R1 = 0.0508$ for 8920 data with $F^2 > 2\sigma\ (F^2)$; $wR_2 = 0.1314$ for all data.[12] A complete set of X-ray crystallographic structural data for compound **2a** (CCDC no. 791781) is available at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk) on request, quoting the deposition number.

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