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On the protonation of a macrobicyclic cage: an inert tribenzylamine fragment and three robust aminophosphonium units

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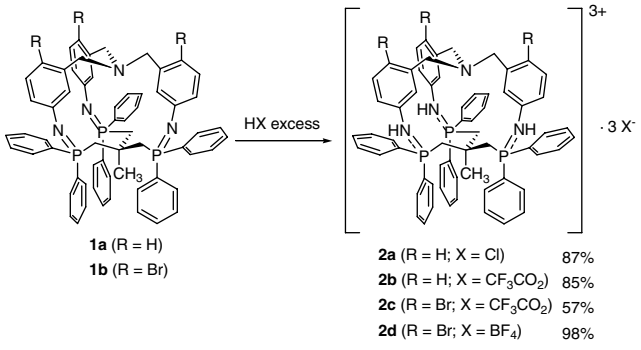
Abstract—The protonation of a macrobicyclic cage with four intracyclic nitrogen atoms (one included into a tribenzylamine fragment and the other three into iminophosphorane units) led to tris(aminophosphonium) cations. In the salts, the three anions are situated outside the internal cavity although intercalated within the grooves of its macrobicyclic skeleton. The three aminophosphonium units are remarkably resistant to hydrolysis.

The protonation of chiral, propeller macrobicycles **1a**[1] and **1b**[2] by a tenfold excess of hydrochloric, trifluoroacetic or tetrafluoroboric acid gave rise to the organic salts **2** in 57–98% yields, as a result of the protonation of the three nitrogen atoms of the iminophosphorane units (Scheme 1).[3] Notably, the pivotal nitrogen included in a tribenzyl amine fragment, bearing an electron lone pair oriented inside the cavity, remained intact in spite of its basicity being presumed to be greater than that of the *N*-aryl iminophosphorane functions. This assumption was reasoned on the basis of the respective pK_a values of trialkylamines (e.g., triethylamine, 10.75 in water)[4] and *N*-aryl iminophosphoranes (7.72 for Ph–N=PPh$_3$ in 76% aqueous EtOH).[5] In fact, triethylamine is usually the preferred base for deprotonating intermediate aminophosphonium salts in the well-known Kirsanov preparation of *N*-aryl iminophosphoranes from primary aryl amines and tertiary phosphane dibromides.[6]



1a (R = H)
1b (R = Br)

2a (R = H; X = Cl) 87%
2b (R = H; X = CF_3CO_2) 85%
2c (R = Br; X = CF_3CO_2) 57%
2d (R = Br; X = BF_4) 98%

Scheme 1. Synthesis of tris(aminophosphonium) salts **2**.

Although protonation of the pivotal nitrogen atom is thermodynamically favourable, its failure in this case is not unprecedented, as a number of examples of kinetically slow, inside protonation of bridgehead nitrogen atoms in cage amines have been reported.[7] In fact, such intracavity proton would not be stabilized by solvent or counter-anions as apparently they cannot enter inside the cavity, which is filled by aryl and methylene protons.

The ^{31}P NMR of compounds **2** show only one singlet close to 30 ppm, which is in the typical range of aminophosphonium salts.[8] The simplicity of these spectra indicates the presence of a C_3 axis, and hence high symmetry.

On the other hand, the intrinsic helical chirality of these species, analogous to that of their precursors, is evidenced by the anisochronous CH_2N and CH_2P methylene protons in their ^{1}H NMR spectra, as well as by the appearance in their ^{13}C NMR spectra of the *ipso*, *ortho*, *meta* and *para* carbons of the *Ph*P rings as two

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Table 1. Relevant ^{1}H NMR chemical shifts of **1a–b** and **2a–d**

Tris(iminophosphoranes)						Tris(aminophosphonium) salts					
Comp.	$\delta(CH_3)$	$\delta(CH_2N)$		$\delta(CH_2P)$		Comp	$\delta(CH_3)$	$\delta(CH_2N)$		$\delta(CH_2P)$	
		H_{eq}	H_{ax}	H_{eq}	H_{ax}			H_{eq}	H_{ax}	H_{eq}	H_{ax}
1a	−0.78	2.94	3.57	3.20	3.97	**2a**	0.83	3.00	3.25	4.96	4.00
						2b	1.12	2.98	3.25	5.03	3.90
1b	−0.69	3.45	3.65	3.23	3.95	**2c**	1.20	3.06	3.65	5.09	3.78
						2d	0.57	3.13	3.72	4.24	3.87

sets of signals. The comparison of the ^{1}H NMR data of the tris(iminophosphoranes) **1** and the salts **2** (Table 1) denote the similarity of chemical shift values between the methylene CH_2N protons of **1** and **2**, indicating that the bridgehead nitrogen was not protonated. By comparison, when we carried out the protonation of tris(*m*-azidobenzyl)amine [$\delta(CH_2) = 3.52$ ppm], the immediate precursor of **1**,[1,2] with hydrochloric acid to give tris(*m*-azidobenzyl)ammonium hydrochloride [$\delta(CH_2) = 4.29$ ppm] the methylene protons of the later were deshielded by 0.77 ppm in relation to the amine.

However, remarkable differences between **1** and **2** are observed in the chemical shift of the protons which are in the lower triphosphane fragment (CH_3 and CH_2P protons in Table 1). For example, the CH_3 protons in the ^{1}H NMR spectrum of **2c** appearing at $\delta = 1.20$ are notably shifted downfield ($\Delta\delta = 1.89$ ppm) from those in **1b** ($\delta = -0.69$ ppm). Also is considerable the change in the shift of the *pseudoequatorial* proton of the CH_2P unit, that appears for example at δ 5.09 ppm in compound **2c**, 1.86 ppm deshielded with respect to **1b**.

Such large differences could be rationalized by an X-ray crystallographic analysis of compound **2b** (Fig. 1).[9]

Relatively strong hydrogen bonds[10] are established between the NH protons and only one oxygen atom of the CF_3COO^- anions placed outside the inner cavity. Such hydrogen bonds were nonsymmetrical and the second oxygen atom of the CF_3COO^- anions established short contacts with the *pseudoequatorial* hydrogens of the CH_2P units. This fact justified the deshielding of the signal corresponding to these last protons in the ^{1}H NMR spectra of **2**. This is a special example of the steric deshielding effect.[11] In Figure 2, a schematic representation of the lower triphosphane fragment of neutral **1a** and ionic **2b** species is presented, remarking these facts.

Obviously, the conversion N=P → HN–P$^+$ involves the enlarging of the N–P bond and confers more flexibility to the bicycle, thus allowing a concerted relaxation in order to accommodate optimum hydrogen bonds to CF_3COO^- and optimum intercalation of these anion within the grooves of the molecule. Two consequences of this relaxation are (a) the average angle H_2C–P–C_i-(Ph_{ax}) changes from 106.5° in **1b** to 111.9° in **2b**, and so the average distance $CH_3\cdots$centroid(Ph_{ax}) increases from 3.784 Å in **1b** to 4.255 Å in **2b**; and (b) the average dihedral angle H_2C–P–C_i(Ph_{ax})–C_o(Ph_{ax}) changes from 60.5° in **1b** to 36.6° in **2b**. These data indicate a remarkable difference in the orientation of the *pseudoaxial* phenyl rings, which are 'facing' the pivotal CH_3 in a lesser extent in **2b** than in **1b**, and, consequently, diminishing

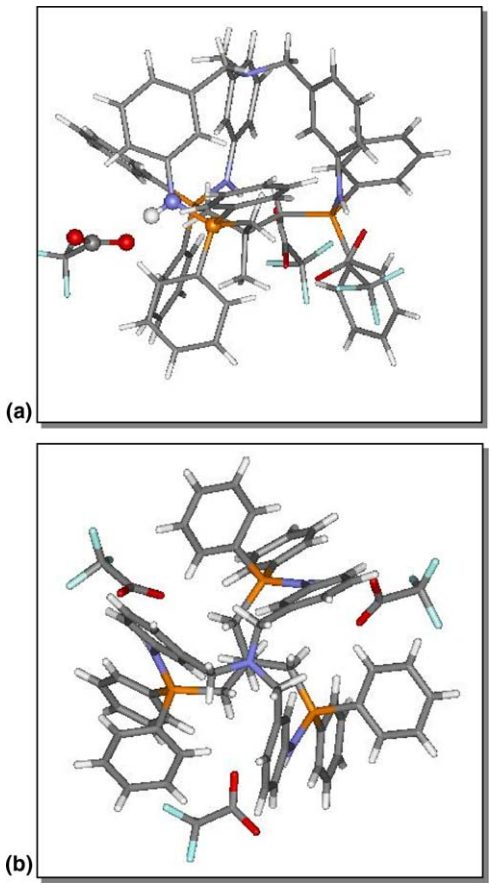

Figure 1. Molecular structure of compound **2b**: (a) an axial view; (b) a perspective view as projected along the threefold axis.

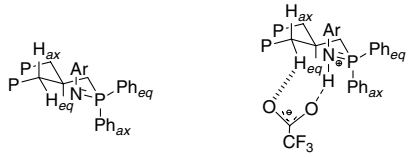

Figure 2. The lower triphosphane fragment of compounds **1b** and **2b**.

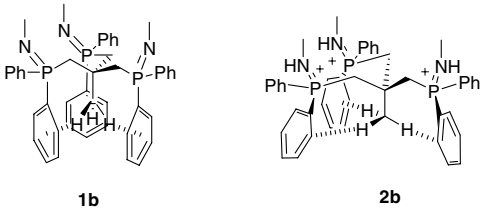

Figure 3. Stabilizing CH···π interactions of pivotal CH_3 in **1b** and **2b**.

the stabilizing CH···π interactions and the shielding of the CH_3 protons in the ^1H NMR spectra (Fig. 3).

The ^1H NMR data of **2b** in $CDCl_3$ solution at 298 K commented above revealed that, probably, the conformation of this compound in solution is similar to that in the solid state. The rest of salts **2** seem to adopt a tridimensional arrangement close to that of **2b**, if we take into account the similarity of their NMR data.

Iminophosphoranes easily undergo acid-catalyzed hydrolysis for yielding the respective amines and phosphane oxides.[12] These processes occur by protonation on nitrogen giving aminophosphonium salts, followed by attack of water on phosphorus. It is surprising in this respect the exceptional stability of aminophosphonium salts **2** in the presence of water. Thus, they remained unaltered when submitted to the usual hydrolysis procedure (aqueous THF, 25 °C, 24 h) but also under harsher conditions (reflux, 48 h).

Finally, the treatment of the tris(aminophosphonium) salt **2a** with an excess of triethylamine in benzene at reflux temperature achieved the triple deprotonation reverting it to the original tris(iminophosphorane) **1a**.

Acknowledgements

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3. *General procedure for the preparation of the triaminophosphonium salts* **2**. The corresponding acid (5 mmol) was added to a solution of the tris(iminophosphorane) **1** (0.5 mmol) in dichloromethane (10 mL). The mixture was stirred for 12 h. The precipitated solid was filtered, washed with cold dichloromethane (3 × 5 mL), dried under vacuum and recrystallized.
Tris(aminophosphonium) trichloride **2a**: Yield: 87%; mp 259–260 °C (colorless prisms from chloroform); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.83$ (s, 3H; CH_3), 3.00 (d, $J(H,H) = 12.6$ Hz, 3H; CH_AH_BN), 3.25 (d, $J(H,H) = 12.6$ Hz, 3H; CH_AH_BN), 4.00 (pseudo t, $J(H,H)(H,P) = 15.5$ Hz, 3H; CH_AH_BP), 4.96 (m, 3H; CH_AH_BP), 6.42 (s, 3H; H_{arom}), 6.80 (d, $J(H,H) = 6.3$ Hz, 3H; H_{arom}), 7.26–7.41 (m, 11H; H_{arom}), 7.63–7.78 (m, 16H; H_{arom}), 8.12 (br s, 3H; H_{arom}), 8.98–9.02 (m, 6H; H_{arom}), 11.99 (br s, 3H; NH); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): $\delta = 28.51$ (CH_3C), 36.59 (m; CH_2P), 43.46 (q, $^2J(C,P) = 3.2$ Hz; CH_3C), 57.31 (CH_2N), 119.17 (d, $^1J(C,P) = 105.0$ Hz; *i*C–PhP), 120.37 (d, $^3J(C,P) = 5.2$ Hz; *s-cis*-CH=C–N=P), 122.01 (d, $^1J(C,P) = 112.3$ Hz; *i*C–PhP), 122.72 (d, $^3J(C,P) = 12.2$ Hz; *s-trans*-CH=C–N=P), 124.32, 129.85 (d, $^3J(C,P) = 13.3$ Hz; *m*C–PhP), 129.93 (d, $^3J(C,P) = 13.9$ Hz; *m*C–PhP), 130.15, 132.52 (d, $^2J(C,P) = 10.4$ Hz; *o*C–PhP), 133.70 (d, $^2J(C,P) = 12.7$ Hz; *o*C–PhP), 134.17 (br s; *p*C–PhP), 134.98 (br s; *p*C–PhP), 139.05 (q), 141.56 (q); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 30.71$; IR (Nujol): $\nu = 3388$ (NH), 1470 (CP), 1118 (NP) cm^{-1}; MS (FAB+): m/z (%) = 951 (100) [$M^+ - 3Cl$]; $C_{62}H_{60}Cl_3N_4P_3$ (1060.45): Calcd C, 70.22; H, 5.70; N, 5.28; found C, 70.13; H, 5.56; N, 5.17.
Tris(aminophosphonium) tris(trifluoroacetate) **2b**: Yield: 85%; mp 258–259 °C (colorless prisms from chloroform/*n*-pentane); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.12$ (s, 3H; CH_3), 2.98 (d, $J(H,H) = 12.6$ Hz, 3H; CH_AH_BN), 3.25 (d, $J(H,H) = 12.6$ Hz, 3H; CH_AH_BN), 3.90 (pseudo t, $J(H,H),(H,P) = 15.5$ Hz, 3H; CH_AH_BP), 5.03 (pseudo quint, $J(H,H),(H,P) = 8.0$ Hz, 3H; CH_AH_BP), 6.36 (s, 3H; H_{arom}), 6.79 (d, $J(H,H) = 7.3$ Hz, 3H; H_{arom}), 7.25–7.32 (m, 9H; H_{arom}), 7.41–7.66 (m, 18H; H_{arom}), 7.96 (d, $J(H,H) = 8.4$ Hz, 3H; H_{arom}), 8.51 (dd, $J(H,H) = 13.9$, 7.3 Hz, 6H; H_{arom}), 11.91 (br s, 3H; NH); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): $\delta = 28.67$ (CH_3C), 35.91 (ddd, $^1J(C,P) = 55.7$ Hz, $^3J(C,P) = 13.1$, 6.0 Hz; CH_2P), 43.13 (q, $^2J(C,P) = 6.4$ Hz; CH_3C), 56.99 (CH_2N), 119.38 (d, $^1J(C,P) = 140.4$ Hz; *i*C–PhP), 119.52 (d, $^3J(C,P) = 4.5$ Hz; *s-cis*-CH=C–N=P), 120.74 (d, $^1J(C,P) = 105.5$ Hz; *i*C–PhP), 121.00 (q, $^1J(C,F) = 309.7$ Hz; CF_3), 122.12 (d, $^3J(C,P) = 11.1$ Hz; *s-trans*-CH=C–N=P), 124.49, 129.81 (d, $^3J(C,P) = 13.3$ Hz; *m*C–PhP), 129.88 (d, $^3J(C,P) = 13.9$ Hz; *m*C–PhP), 130.37, 131.50 (d, $^2J(C,P) = 10.7$ Hz; *o*C–PhP), 132.44 (d, $^2J(C,P) = 12.4$ Hz; *o*C–PhP), 134.18 (d, $^4J(C,P) = 2.2$ Hz; *p*C–PhP), 135.21 (d, $^4J(C,P) = 2.6$ Hz; *p*C–PhP), 139.23 (q), 141.60 (q), 161.77 (q, $^2J(C,F) = 35.0$ Hz; CO); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 30.45$; IR (Nujol): $\nu = 3459$ (NH), 1465 (CP), 1117 (NP) cm^{-1}; MS (FAB+): m/z (%) = 951 (100) [$M^+ - 3CF_3CO_2$]; $C_{68}H_{60}F_9N_4O_6P_3$ (1293.13): Calcd C, 63.16; H, 4.68; N, 4.33; found C, 63.05; H, 4.78; N, 4.46.
Tris(aminophosphonium) tris(trifluoroacetate) **2c**: Yield: 57%; mp >350 °C(colorless prisms from chloroform/diethyl ether); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ (s, 3H; CH_3), 3.06 (d, $J(H,H) = 13.4$ Hz, 3H; CH_AH_BN), 3.65 (d, $J(H,H) = 13.4$ Hz, 3H; CH_AH_BN), 3.78 (pseudo t, $J(H,H),(H,P) = 16.2$ Hz, 3H; CH_AH_BP), 5.09 (pseudo quint, $J(H,H),(H,P) = 6.9$ Hz, 3H; CH_AH_BP), 6.42 (d, $J(H,H) = 2.7$ Hz, 3H; H_{arom}), 7.29–7.36 (m, 6H; H_{arom}), 7.47–7.60 (m, 18H; H_{arom}), 7.66–7.69 (m, 3H; H_{arom}), 7.86 (dd, $J(H,H) = 8.7$, 2.7 Hz, 3H; H_{arom}), 8.45 (dd, $J(H,H) = 14.3$, 7.4 Hz, 6H; H_{arom}), the resonance of the NH is not observed; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): $\delta = 30.42$ (CH_3C), 35.81 (m; CH_2P), 43.19 (q, $^2J(C,P) = 5.0$ Hz; CH_3C), 55.70 (CH_2N), 118.90 (d, $^1J(C,P) = 121.8$ Hz; *i*C–PhP), 119.01, 120.39 (q, $^1J(C,F) = 285.5$ Hz; CF_3), 120.41 (d, $^1J(C,P) = 105.8$ Hz; *i*C–PhP), 121.12 (d, $^3J(C,P) = 1.0$ Hz; *s-cis*-CH=C–N=P), 123.80 (d, $^3J(C,P) = 11.0$ Hz; *s-trans*-CH=C–N=P), 130.03 (d, $^3J(C,P) = 14.5$ Hz; *m*C–PhP), 130.05 (d, $^3J(C,P) = 12.3$ Hz; *m*C–PhP), 131.30 (d, $^2J(C,P) = 10.4$ Hz; *o*C–PhP), 132.34 (d, $^2J(C,P) = 12.2$ Hz; *o*C–PhP), 134.68, 134.70 (br s, *p*C–PhP), 135.51 (br s, *p*C–PhP), 138.42 (q), 139.93 (q), 161.54 (q, $^2J(C,F) = 36.6$ Hz,

CO); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 30.09$; IR (Nujol): $\nu = 3411$ (NH), 1463 (CP), 1116 (NP) cm^{-1}; MS (FAB+): m/z (%) = 1191 (42) $[M^+ + 4 - 3CF_3CO_2]$, 1189 (100) $[M^+ + 2 - 3CF_3CO_2]$, 1188 (66) $[M^+ + 1 - 3CF_3CO_2]$, 1187 (93) $[M^+ - 3CF_3CO_2]$; $C_{68}H_{57}Br_3F_9N_4O_6P_3$ (1529.82): Calcd C, 53.39; H, 3.76; N, 3.66; found C, 53.25; H, 3.66; N, 3.53.

Tris(aminophosphonium) tris(tetrafluoroborate) **2d**: Yield: 98%; mp >350 °C (colorless prisms from chloroform/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.57$ (s, 3H; CH_3), 3.13 (d, $J(H,H) = 13.4$ Hz, 3H; CH_AH_BN), 3.72 (d, $J(H,H) = 13.4$ Hz, 3H; CH_AH_BN), 3.87 (pseudo t, $J(H,H),(H,P) = 15.7$ Hz, 3H; CH_AH_BP), 4.24 (pseudo quint, $J(H,H),(H,P) = 8.1$ Hz, 3H; CH_AH_BP), 6.43 (d, $J(H,H) = 2.6$ Hz, 3H; H_{arom}), 7.44–7.51 (m, 12H; H_{arom}), 7.61–7.73 (m, 18H; H_{arom}), 8.20–8.28 (m, 6H; H_{arom}), 8.34 (d, $^{2}J(H,P) = 10.5$ Hz, 3H; NH); $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): $\delta = 28.65$ (CH_3C), 36.03 (m; CH_2P), 41.20 (q, $^{2}J(C,P) = 5.8$ Hz; CH_3C), 55.90 (CH_2N), 116.93 (d, $^{1}J(C,P) = 100.8$ Hz; *i*C–PhP), 119.28 (d, $^{1}J(C,P) = 100.7$ Hz; *i*C–PhP), 119.47, 119.89 (d, $^{3}J(C,P) = 3.3$ Hz; *s-cis-C*H=C–N=P), 122.99 (d, $^{3}J(C,P) = 9.9$ Hz; *s-trans-C*H=C–N=P), 130.57 (d, $^{3}J(C,P) = 13.6$ Hz; *m*C–PhP), 130.93 (d, $^{3}J(C,P) = 14.3$ Hz; *m*C–PhP), 131.63 (d, $^{2}J(C,P) = 11.2$ Hz; *o*C–PhP), 131.88 (d, $^{2}J(C,P) = 13.9$ Hz; *o*C–PhP), 135.19 (d, $^{4}J(C,P) = 1.3$ Hz), 135.31 (d, $^{4}J(C,P) = 2.5$ Hz; *p*C–PhP), 135.76 (d, $^{4}J(C,P) = 2.8$ Hz; *p*C–PhP), 137.12 (q), 140.15 (q); $^{31}P\{^{1}H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta = 31.83$; IR (Nujol): $\nu = 3180$ (NH), 1489 (CP), 1115 (NP) cm^{-1}; MS (FAB+): m/z (%) = 1191 (89) $[M^+ + 4 - 3BF_4]$, 1189 (100) $[M^+ + 2 - 3BF_4]$, 1187 (62) $[M^+ - 3BF_4]$; $C_{62}H_{57}B_3Br_3F_{12}N_4P_3$ (1451.19): Calcd C, 51.31; H, 3.96; N, 3.86; found C, 51.42; H, 3.84; N, 3.81.

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9. Crystal data for **2b**: Empirical formula, $C_{69}H_{60}F_9N_4O_6P_3$ (+148.75 e^- as solvent); formula weight, 1453.87; uncoloured, rectangular crystals; crystal size $0.40 \times 0.20 \times 0.20$ mm^3; triclinic; $a = 13.000(16)$ Å, $b = 21.559(2)$ Å, $c = 27.366(3)$ Å; $\alpha = 81.513(3)$; $\beta = 83.115(3)$; $\gamma = 81.257(3)$; $V = 7460.3(14)$ $Å^3$; space group, P-1; $Z = 4$; $D_{calcd} = 1.283$ g/cm^3; $F_{000} = 3299$; λ (Mo K_α) = 0.71073 Å; $R(I \geqslant 2\sigma_1) = 0.0577$, $wR^2 = 0.1245$. Detailed X-ray crystallographic data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/data_request/cif (CCDC No. 172791).
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