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Intramolecular Hydrogen Bonded Tertiary Phosphines as 1,3,5-Triaza-7-phosphaadamantane (PTA) Analogues

Allen T. Ekubo, Mark R. J. Elsegood, Andrew J. Lake and Martin B. Smith*

Department of Chemistry, Loughborough University, Loughborough, Leics,

LE11 3TU, UK

* To whom correspondence should be addressed. E-mail: m.b.smith@lboro.ac.uk. Tel: +44 (0)1509 222553. Fax: +44 (0)1509 223925.
Abstract—New cationic trialkylphosphines \([\text{P(CH}_2\text{NH}_2\text{R})\{\text{CH}_2\text{N(R)CH}_2\text{N(R)CH}_2\}]^+\) (R = C\(_6\)H\(_5\)CH\(_2\) a; 4-FC\(_6\)H\(_4\)CH\(_2\) b), as their Cl\(^-\) (1a, 1b), SbF\(_6\)\(^-\) (2a, 2b) and PF\(_6\)\(^-\) (3a, 3b) salts, are described. The phosphine framework is conformational locked, in the solid state, through pairs of intramolecular N–H···N hydrogen-bonds which are maintained in the Ru\(^{II}\) and Rh\(^{III}\) complexes 4 and 5. Phosphines 1a–3b can be considered as charged variants of the well known PTA ligand.
The ability by which tertiary phosphines can be modified undoubtedly remains a major reason why this ligand class continues to find spectacular success in many branches of chemistry. Considerable recent interest has focused on the aliphatic caged tertiary phosphine 1,3,5-triaza-7-phosphaadamantane (hereafter abbreviated PTA) which has been shown to possess many desirable attributes including water solubility.\textsuperscript{1} Synthetic routes for modifying the adamantanoid framework of PTA such as protonation/alkylation of the tertiary nitrogen atoms or upper/lower rim functionalization have been reported.\textsuperscript{2,3} Consequently numerous applications of PTA and their derivatives in biomedicine,\textsuperscript{4} coordination and organometallic chemistry\textsuperscript{4,5} and catalysis,\textsuperscript{6} especially in aqueous media, have been realized. One aspect of PTA not previously investigated is the ability to manipulate the nitrogen centers by, for example, changing the alkyl/aryl substituents yet \textit{preserve} the tertiary amine character as opposed to quaternization\textsuperscript{3b} or forming boronated species.\textsuperscript{5c} One approach by which this could be accomplished is to envisage removal of two “upper-rim” methylene ($\text{N}^-$CH$_2$-$\text{N}$) groups from PTA thereby allowing different R groups on nitrogen to be incorporated. Using suitable non-covalent interactions, such as intramolecular H-bonding, would allow for retention of the adamantane core. As part of ongoing studies in our group we have recently developed highly functionalized (di)tertiary phosphines with regiospecific H-bonding capabilities.\textsuperscript{7} Herein a simple concept for the synthesis of novel cationic trialkylphosphines, with similar stereoelectronic properties to PTA, and a preliminary exploration of their late transition metal chemistry are reported. All new compounds have been characterized by a combination of spectroscopic and single crystal X-ray diffraction techniques.
Experimental Section

Materials. All manipulations and reactions were carried out under aerobic conditions. Dichloromethane was previously distilled over CaH₂, diethyl ether over sodium/benzophenone and tetrakis(hydroxymethyl)phosphonium chloride (THPC) was recrystallized from 2-propanol before use. All other solvents and chemicals were obtained from commercial suppliers and used without further purification. The dinuclear metal compounds {RuCl₂(η⁶-p-cymene)}₂ and {RhCl₂(η⁵-Cp*)}₂ were prepared according to published procedures.

Instrumentation. FT–IR spectra were recorded within pressed KBr pellets over the range 4000–200 cm⁻¹ using a Perkin-Elmer system 2000 FT spectrometer. ¹H NMR and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external TMS or 85% H₃PO₄. Coupling constants (J) in Hz. All NMR spectra were recorded in dmsο-d⁶ solutions at ca. 298 K. Elemental analyzes (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Mass spectra for 1a–5 were analyzed (JEOL SX102 instrument) by fast atom bombardment (FAB) in a positive ionization mode using a 3-nitrobenzyl alcohol (NOBA) matrix. Compounds 6a and 6b were analyzed (Finnigan MAT 95XP) by low-resolution FAB (LSIMS) in positive ionization mode using CH₂Cl₂ as the solvent and a NOBA matrix.

Preparation of 1a. To a solution of THPC (3.83 g, 20.1 mmol) in EtOH (100%, 75 ml) was added dropwise C₆H₅CH₂NH₂ (8.94 g, 83.4 mmol). During the addition heat was generated and thick white fumes were observed. After ca. 5 min the solution became clear. The mixture was stirred for 2 h at room temperature (frequently some unwanted “sticky” material was formed which was separated from the solution by decantation) and the volume reduced on a rotary evaporator to approx. a quarter of the original volume. The resulting crystalline solid was filtered and dried under vacuum. Yield: 7.60 g
(86%). Selected data: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $-55.0$ ppm. $^{1}\text{H}$ NMR: $9.55$ (br, NH$_2$, 2H), $7.59-7.01$ (m, arom. H, 15H), $4.21$ (s, CH$_2$, 2H), $3.42-3.38$ (m, CH$_2$, 8H), $3.18$ (d, $^{2}J_{PH}$ 13.6, CH$_2$, 2H), $2.65$ (t, CH$_2$, 2H) ppm. FT–IR: 3028 and 2781 (br, NH and CH) cm$^{-1}$. FAB–MS: $m/z$ 404 [M – Cl]. Anal. Calcd. for C$_{25}$H$_{31}$N$_{3}$PCl: C, 68.24; H, 7.12; N, 9.55. Found: C, 68.25; H, 7.10; N, 9.58.

**Preparation of 1b.** To a solution of THPC (2.85 g, 14.9 mmol) in EtOH (100%, 55 ml) was added dropwise 4-FC$_6$H$_4$CH$_2$NH$_2$ (7.77 g, 62.0 mmol). The mixture was stirred for 2 h at room temperature and the volume reduced on a rotary evaporator to approx. a quarter of the original volume. The resulting crystalline solid was filtered and dried under vacuum. Additional crops of 1b were obtained when the filtrate was allowed to stand for more than 24 h. Yield: $6.11$ g (83%). Selected data: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $-55.2$ ppm. $^{1}\text{H}$ NMR: $7.62-6.93$ (m, arom. H, 12H), $4.21$ (s, CH$_2$, 2H), $3.29$ (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH$_2$), $3.18$ (d, $^{2}J_{PH}$ 13.8, CH$_2$, 2H), $2.67$ (t, CH$_2$, 2H) ppm. FT–IR: 3044 and 2821 (br, NH and CH) cm$^{-1}$. FAB–MS: $m/z$ 458 [M – Cl]. Anal. Calcd. for C$_{25}$H$_{28}$F$_3$N$_3$PCl: C, 60.78; H, 5.73; N, 8.51. Found: C, 60.56; H, 5.58; N, 8.41.

**Preparation of 2a.** A solution of Na(SbF$_6$) (0.18 g, 0.69 mmol) in the minimum volume of HPLC grade CH$_3$OH was added to a solution of 1a (0.20 g, 0.45 mmol) in HPLC grade CH$_3$OH (10 ml). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: $0.28$ g (97%). Selected data: $^{31}\text{P}\{^{1}\text{H}\}$ NMR: $-55.2$ ppm. $^{1}\text{H}$ NMR: $9.01$ (br, NH$_2$, 2H), $7.49-6.92$ (m, arom. H, 15H), $4.22$ (s, CH$_2$, 2H), $3.57-3.41$ (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH$_2$), $3.10$ (d, $^{2}J_{PH}$ 12, CH$_2$, 2H), $2.66$ (t, CH$_2$, 2H) ppm. FT–IR: 3064, 3031 and 2808 (s, NH and CH), 654 (vs, SbF) cm$^{-1}$. FAB–MS: $m/z$ 404 [M –
Preparation of 2b. A solution of Na(SbF$_6$) (0.16 g, 0.61 mmol) in the minimum volume of HPLC grade CH$_3$OH was added to a solution of 1b (0.20 g, 0.40 mmol) in HPLC grade CH$_3$OH (10 ml). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.21 g (73%). Selected data: $^{31}$P{$^1$H} NMR: −55.0 ppm. $^1$H NMR: 8.95 (br, NH$_2$, 2H), 7.57−6.98 (m, arom. H, 12H), 4.22 (s, CH$_2$, 2H), 3.84−3.50 (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH$_2$), 3.10 (d, $^2$J$_{PH}$ 13.6, CH$_2$, 2H), 2.67 (t, CH$_2$, 2H) ppm. FT−IR: 3052, 2953, 2830, 2799 and 2730 (m, NH and CH), 653 (vs, SbF) cm$^{-1}$. FAB−MS: m/z 458 [M − SbF$_6$]. Anal. Calcd. for C$_{25}$H$_{28}$N$_3$PSbF$_9$·0.5H$_2$O: C, 42.70; H, 4.16; N, 5.98. Found: C, 42.46; H, 3.90; N, 5.87.

Preparation of 3a. A solution of K(PF$_6$) (0.13 g, 0.71 mmol) in the minimum volume of HPLC grade CH$_3$OH was added to a solution of 1a (0.20 g, 0.45 mmol) in HPLC grade CH$_3$OH (10 ml). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.18 g (72%). Selected data: $^{31}$P{$^1$H} NMR: −54.6, −144.2 ppm, $^1$J$_{PF}$ 711 (PF$_6^-$). $^1$H NMR: 9.02 (br, NH$_2$, 2H), 7.49−7.01 (m, arom. H, 15H), 4.23 (s, CH$_2$, 2H), 3.85−3.41 (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH$_2$), 3.10 (d, $^2$J$_{PH}$ 14, CH$_2$, 2H), 2.67 (t, CH$_2$, 2H) ppm. FT−IR: 3030 and 2809 (w, NH and CH), 842 (vs, PF) cm$^{-1}$. FAB−MS: m/z 404 [M − PF$_6$]. Anal. Calcd. for C$_{25}$H$_{31}$N$_3$P$_2$F$_6$: C, 54.64; H, 5.70; N, 7.65. Found: C, 55.03; H, 5.61; N, 7.68.
**Preparation of 3b.** A solution of K(PF$_6$) (0.11 g, 0.60 mmol) in the minimum volume of HPLC grade CH$_3$OH was added to a solution of 1b (0.20 g, 0.40 mmol) in HPLC grade CH$_3$OH (10 ml). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.20 g (83%). Selected data: $^3$P{$^1$H} NMR: -54.4, -144.2 ppm, $^1$J$_{PF}$ 714 (PF$_6^-$).

$^1$H NMR: 9.00 (br, NH$_2$, 2H), 7.58–6.98 (m, arom. H, 12H), 4.22 (s, CH$_2$, 2H), 3.84–3.51 (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH$_2$), 3.12 (d, $^2$J$_{PH}$ 13.6, CH$_2$, 2H), 2.67 (t, CH$_2$, 2H) ppm. FT–IR: 3077, 3042, 3007, 2949, 2820 (m, NH and CH), 848 (vs, PF) cm$^{-1}$. FAB–MS: $m/z$ 458 [M – PF$_6$]. Anal. Calcd. for C$_{25}$H$_{28}$N$_3$P$_2$F$_9$·H$_2$O: C, 48.32; H, 4.88; N, 6.76. Found: C, 48.21; H, 4.51; N, 6.72.

**Preparation of RuCl$_2$(η$^6$-p-cymene)(2a) (4).** To a stirred solution of {RuCl$_2$(η$^6$-p-cymene)}$_2$ (0.030 g, 0.049 mmol) in CH$_2$Cl$_2$ (10 ml) was added 2a (0.063 g, 0.10 mmol) as a solid in one portion. The solution was stirred for 30 min, the volume reduced to ca. 1–2 ml under reduced pressure and Et$_2$O (10 ml) added. The suspension was stirred for 30 min and the solid collected on a glass sinter and dried under vacuum. Yield: 0.080 g (91%). Selected data: $^3$P{$^1$H} NMR: 7.3 ppm. $^1$H NMR: 8.98 (br, NH$_2$, 2H), 7.53–6.99 (m, arom. H, 15H), 5.94 (dd, $^3$J$_{PH}$ 8, C$_6$H$_4$, 4H), 4.29 (s, CH$_2$, 2H), 4.02 (d, $^2$J$_{PH}$ 4.8, CH$_2$, 2H), 3.80–3.71 (m, CH$_2$, 4H), 3.45 (partially obscured by solvent, CH$_2$), 2.62 (sept, $^3$J$_{PH}$ 6.8, CH(CH$_3$)$_2$, 1H), 1.96 (CH$_3$, 3H), 1.14 (d, $^3$J$_{PH}$ 6.8, CH(CH$_3$)$_2$, 6H) ppm. FT–IR: 3060 and 2967 (w, NH and CH), 660 (vs, SbF) cm$^{-1}$. FAB–MS: $m/z$ 710 [M – SbF$_6$]. Anal. (bulk material) Calcd. for C$_{35}$H$_{45}$N$_3$PSbF$_6$RuCl$_2$·3.5CH$_2$Cl$_2$: C, 37.18; H, 4.22; N, 3.38. Found: C, 37.17; H, 4.00; N, 3.24. A single crystal X-ray determination of 4 showed 1.67 CH$_2$Cl$_2$ molecules present in the crystal lattice.
Preparation of \( \text{RhCl}_2(\eta^5\text{-Cp}^*)(2a) \) (5). To a stirred solution of \{\text{RhCl}_2(\eta^5\text{-Cp}^*)\}_2 \leq 0.030 \text{ g}, 0.050 \text{ mmol}\) in CH\(_2\)Cl\(_2\) (10 ml) was added 2a \leq 0.062 \text{ g}, 0.10 \text{ mmol}\) as a solid in one portion. The solution was stirred for 30 min, the volume reduced to ca. 1–2 ml under reduced pressure and Et\(_2\)O (10 ml) added. The suspension was stirred for 30 min and the solid collected on a glass sinter and dried under vacuum. Yield: 0.090 g (98%). Selected data: \( ^{31}\text{P}\{^1\text{H}\} \text{ NMR}: 4.6 \text{ ppm}, ^{1}\text{J}_{\text{RhP}} 144. ^{1}\text{H NMR}: 7.51–6.91 \) (m, arom. H, 15H), 4.37 (s, CH\(_2\), 2H), 4.10 (s, CH\(_2\), 2H), 3.76 (d, \( ^{2}\text{J}_{\text{P-H}} 12.4, \text{CH}_2\), 4H), 3.22 (multiplicity could not fully be assigned due to overlap with residual solvent peaks, CH\(_2\)), 1.67 (s, \( \eta^5\text{-Cp}^* \), 15H) ppm. FT–IR: 3031 (br, NH and CH), 660 (vs, SbF) cm\(^{-1}\). FAB–MS: \( m/z \) 712 [M – SbF\(_6\)]. Anal. (bulk material) Calcd. for C\(_{35}\)H\(_{46}\)N\(_3\)PSbF\(_6\)RhCl\(_2\)·CH\(_2\)Cl\(_2\): C, 41.81; H, 4.68; N, 4.06. Found: C, 41.46; H, 4.50; N, 4.07. A single crystal X-ray determination of 5 showed two CH\(_2\)Cl\(_2\) molecules present in the crystal lattice.

Preparation of \( \text{trans-RhCl(CO)}(\text{1a})_2 \) (6a). To a stirred solution of \{\text{RhCl(CO)}\}_2 \leq 0.030 \text{ g}, 0.080 \text{ mmol}\) in CH\(_2\)Cl\(_2\) (10 ml) was added 1a \leq 0.14 \text{ g}, 0.32 \text{ mmol}\) as a solid in one portion. The dark orange solution immediately went pale yellow and a yellow solid deposited within ca. 10 min. The suspension was stirred for 30 min, the volume reduced to ca. 1–2 ml under reduced pressure and Et\(_2\)O (10 ml) added. The solid was collected on a glass sinter and dried under vacuum. Yield: 0.14 g (88%). Due to the extreme insolubility of 6a in both non polar and polar solvents no meaningful NMR (\( ^1\text{H}, ^{31}\text{P} \)) data could be obtained for this compound. FT–IR: 1979 (CO) cm\(^{-1}\). LSI–MS: \( m/z \) 1009 [M – 2H – Cl]. Anal. Calcd. for C\(_{51}\)H\(_{62}\)N\(_6\)OP\(_2\)RhCl\(_3\)·1.25CH\(_2\)Cl\(_2\): C, 54.45; H, 5.65; N, 7.29. Found: C, 54.28; H, 5.40; N, 7.46.

Preparation of \( \text{trans-RhCl(CO)}(\text{1b})_2 \) (6b). To a stirred solution of \{\text{RhCl(CO)}\}_2 \leq 0.030 \text{ g}, 0.080 \text{ mmol}\) in CH\(_2\)Cl\(_2\) (10 ml) was added 1b \leq 0.15 \text{ g}, 0.30 \text{ mmol}\) as a solid in one portion. The dark orange
solution immediately went pale yellow and a yellow solid deposited within ca. 10 min. The suspension was stirred for 30 min, the volume reduced to ca. 1–2 ml under reduced pressure and Et₂O (10 ml) added. The solid was collected on a glass sinter and dried under vacuum. Yield: 0.16 g (93%). Due to the extreme insolubility of 6b in both non polar and polar solvents no meaningful NMR (¹H, ³¹P) data could be obtained for this compound. FT–IR: 1979 (CO) cm⁻¹. LSI–MS: m/z 1117 [M – 2H – Cl]. Anal. Calcd. for C₅₁H₅₆N₆OP₂F₆RhCl₃·CH₂Cl₂: C, 50.40; H, 4.72; N, 6.78. Found: C, 50.63; H, 4.70; N, 6.94.

X-ray crystallography. Suitable crystals of 1b were obtained by allowing an ethanol filtrate, obtained from the reaction of THPC with 4-FC₆H₄CH₂NH₂, to stand for several days. Crystals of 2b and 3a were obtained upon layering a CH₂Cl₂ solution with petroleum ether (b.p. 40–60 °C) over several days. Slow diffusion of petroleum ether (b.p. 40–60 °C) into a CDCl₃/CH₂Cl₂ solution gave X-ray quality crystals of 4·1.67CH₂Cl₂. Vapor diffusion of Et₂O into a CH₂Cl₂ solution gave suitable crystals of 5·2CH₂Cl₂.

Measurements for 1b, 2b, 3a and 4·1.67CH₂Cl₂ were made on a Bruker Apex 2 CCD diffractometer, at 150 K, using graphite-monochromated radiation from a sealed tube Mo–Kα source (λ = 0.71073 Å). Diffraction data for 5·2CH₂Cl₂ was collected, at 153 K, using a rotating anode source and a Bruker-Nonious Roper CCD camera. Narrow frame ω-scans were employed for 1b, 2b, 3a and 4·1.67CH₂Cl₂, φ and ω-scans were used for 5·2CH₂Cl₂. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for 4·1.67CH₂Cl₂) and refined on F² values for all unique data by full-matrix least-squares. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically. NH hydrogens for 2b, 3a and 4 had coordinates freely refined with Ueq set to 1.2Ueq of the carrier atom, whilst the remaining hydrogen coordinates were constrained using a riding model with Ueq set to 1.2Ueq.
of the carrier atom (1.5$U_{eq}$ for methyl hydrogen). In 4·1.67CH$_2$Cl$_2$, one of the CH$_2$Cl$_2$ molecules was modeled as disordered over two sets of positions. This disorder was refined with restraints on geometry and anisotropic displacement parameters. Major component = 66.0(3)%. In 5·2CH$_2$Cl$_2$, the SbF$_6^-$ counter ion was found to be disordered over two sets of positions and was refined as above; major component = 80.7(5)%. Programs used were COLLECT$^{11}$ or Bruker AXS APEX 2$^{12}$ for diffractometer control and DENZO$^{13}$ or SAINT$^{14}$ for frame integration, Bruker SHELXTL$^{15,16}$ for structure solution, refinement and molecular graphics and local programs. Disordered molecules of CH$_2$Cl$_2$ (for 5·2CH$_2$Cl$_2$) were modeled by the Platon Squeeze procedure.$^{17}$
Table 1. Details of the X-ray data collections and refinements for compounds 1b, 2b, 3a, 4·1.67CH₂Cl₂ and 5·2CH₂Cl₂.

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<th>3a</th>
<th>4·1.67CH₂Cl₂</th>
<th>5·2CH₂Cl₂</th>
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<td>R(int)</td>
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<td>0.0227</td>
<td>0.0291</td>
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<td>R1 [F² &gt; 2σ(F²)]</td>
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<td>0.0259</td>
<td>0.0377</td>
<td>0.0377</td>
<td>0.0830</td>
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<td>wR2 [all data]</td>
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<td>0.0675</td>
<td>0.1091</td>
<td>0.1033</td>
<td>0.2031</td>
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<tr>
<td>largest difference map features/eÅ³</td>
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<td>0.838, −0.759</td>
<td>0.408, −0.316</td>
<td>1.863, −1.184</td>
<td>1.389, −0.648</td>
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</table>

ªR1 = ∑||F₀|−|Fᶜ||/∑|F₀|. b wR2 = [∑[w(F₀²)² - Fᶜ²)²]²/∑[w(F₀²)]²]¹/².
Results and Discussion

Commercially available tetrakis(hydroxymethyl)phosphonium chloride (THPC, [P(CH₂OH)₄]Cl) has previously been shown to react with primary aromatic amines, through a series of condensation and elimination steps, to give aniline based tertiary phosphines.⁸,¹⁸ In contrast we have found when more basic benzylic amines such as C₆H₅CH₂NH₂ and 4-FC₆H₄CH₂NH₂ are reacted with THPC (ca. 4:1 ratio), crystalline cationic chloride salts 1a and 1b are obtained in high yields (typical non-optimized yields >80%, Scheme 1). Using this procedure we have successfully synthesized batches of 1a at the 5–10 g scale. Anion metathesis of 1a or 1b with Na(SbF₆) or K(PF₆) in CH₃OH at r.t. gave the corresponding salts 2a–3b in excellent yields (72–97%). Compounds 1a–3b have been fully characterized by spectroscopic and analytical methods. In particular, the ³¹P{¹H} NMR spectra (dmsod₆) of 1a–3b showed a single phosphorus resonance around δP ~55, some 40 ppm downfield with respect to PTA [δP ~96.2, D₂O].²ᵃ At ambient temperature 1a–3b possess good solubility in CH₂Cl₂, CH₃OH and dmsod but were found to be insoluble in H₂O. Furthermore, in the solid state 1a–3b are air stable, but slowly oxidize in dmsod₆ solution over ca. 24 h.

Scheme 1 Preparation of salts 1a–3b.ᵃ

```
\[\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{HO} & \quad \text{HO} \\
\text{P} & \quad \text{OH} \\
\text{R} & \quad \text{Cl}^- \\
\text{R} & \quad \text{Cl}^- \\
\text{R} & \quad \text{Cl}^- \\
\text{R} & \quad \text{Cl}^- \\
\end{align*}\]

(i) 4.1 equiv C₆H₅CH₂NH₂ or 4.2 equiv 4-FC₆H₄CH₂NH₂, C₂H₅OH
(ii) Na(SbF₆) or K(PF₆), CH₃OH.
```

ᵃKey: Reagents and conditions: (i) 4.1 equiv C₆H₅CH₂NH₂ or 4.2 equiv 4-FC₆H₄CH₂NH₂, C₂H₅OH
(ii) Na(SbF₆) or K(PF₆), CH₃OH.
The X-ray structures of 1b (Figure 1), 2b (Supporting Information) and 3a (Figure 2) have been determined. Compound 1b was found to lie across a crystallographic mirror plane that bisects the ammonium group of the cation and the methylene diamine bridge (mirror plane runs through P1/C1/N1/C2/C3/C6/F1/C8). Inspection of the intracage P–C bond lengths and P–C–N bond angles reveals close similarities with those of PTA.\textsuperscript{19} The C–P–C angles within the P–C–N–C–N–C ring in 1b, 2b and 3a are in the range 97.78(5)–99.4(2)\textdegree{} and slightly enlarged in comparison with PTA [C–P–C 96.1(1)\textdegree{}]\textsuperscript{19}. The most significant structural feature observed in 1b, 2b and 3a is the presence of a pair of intramolecular hydrogen-bonds between N(1)–H(1A)···N(2) and N(1)–H(1B)···N(3) [1b, N(1)···N(2) 2.915(5) Å, H(1B)···N(2) 2.27 Å, N(1)–H(1B)···N(2) 126\textdegree{}, 2b, N(1)···N(2) 2.804(3) Å, H(1A)···N(2) 2.14(3) Å, N(1)–H(1A)···N(2) 138(3)\textdegree{} and N(1)···N(3) 2.841(3) Å, H(1B)···N(3) 2.20(3) Å, N(1)–H(1B)···N(3) 130(2)\textdegree{}, 3a, N(1)···N(2) 2.8506(13) Å, H(1A)···N(2) 2.241(15) Å, N(1)–H(1A)···N(2) 128.7(12)\textdegree{} and N(1)···N(3) 2.8234(13) Å, H(1B)···N(3) 2.154(15) Å, N(1)–H(1B)···N(3) 132.9(12)\textdegree{}]. Various additional weak intermolecular H-bonding contacts exist between the cations and Cl\textsuperscript{−}, SbF\textsubscript{6}\textsuperscript{−} or PF\textsubscript{6}\textsuperscript{−} counter ions leading to infinite 1-D chains or 2-D sheet structures (Supporting Information for further details).

The single crystal data highlight three key findings regarding the N–H···N hydrogen-bonded framework\textsuperscript{20} in the cations of 1b, 2b and 3a, namely (i) while all synthetic reactions were performed in alcohol solvents (CH\textsubscript{3}OH or C\textsubscript{2}H\textsubscript{5}OH), or required water for precipitation, no disruption of the N–H···N intramolecular hydrogen-bonded motif was apparent under the experimental/crystallization conditions employed, (ii) the core structure of each cation is independent of counter anion (Cl\textsuperscript{−}, SbF\textsubscript{6}\textsuperscript{−} or PF\textsubscript{6}\textsuperscript{−}) even though the potential for alternate hydrogen-bonding arrangements involving these anions is possible, and (iii) the absence of N–H···F–C contacts, albeit rarely observed\textsuperscript{21}, shows that the three electronegative fluorines in the 4-position (1b and 2b) do not disrupt the N–H···N hydrogen-bonding array found here.
Figure 1. (a) ORTEP of the cation in 1b. Selected bond lengths (Å) and angles (deg). P(1)–C(1) 1.841(5), P(1)–C(7) 1.847(3). P(1)–C(1)–N(1) 116.2(3), P(1)–C(7)–N(2) 113.8(2). Thermal ellipsoids are drawn at the 50% probability level. (b) Packing plot of 1b viewed along the c-axis showing the H-bonded sheet pattern.

Figure 2. (a) ORTEP of the cation in 3a. Selected bond lengths (Å) and angles (deg). P(1)–C(1) 1.8490(12), P(1)–C(9) 1.8359(12), P(1)–C(10) 1.8366(13). P(1)–C(1)–N(1) 116.70(7), P(1)–C(9)–N(2) 114.09(7), P(1)–C(10)–N(3) 113.53(7). Thermal ellipsoids are drawn at the 50% probability level. (b) Packing plot of 3a viewed along the c-axis showing the 1-D chain pattern.
Dyson and co-workers\textsuperscript{4h,4j} have previously shown that half-sandwich organometallic \( \text{Ru}^{\text{II}} \) and \( \text{Rh}^{\text{III}} \) compounds of PTA can be synthesized. In order to assess whether \textbf{2a} could function as a similar \( P \)-monodentate ligand, the piano-stool complexes \textbf{4} and \textbf{5} were prepared in high yields. Reassuringly the coordination chemical shifts for \textbf{4} (\( \Delta \delta_P \) 62 ppm) and \textbf{5} (\( \Delta \delta_P \) 60 ppm) were found to closely match those of \( \text{RuCl}_2(\eta^6-p\text{-cymene})(\text{PTA}) \) (\( \Delta \delta_P \) 60 ppm) and \( \text{RhCl}_2(\eta^5-\text{Cp}^*)(\text{PTA}) \) (\( \Delta \delta_P \) 65 ppm)\textsuperscript{4h,4j} suggesting comparable stereoelectronic properties.

\[
\begin{align*}
\text{4} & \quad + \quad \text{SbF}_6^- \\
\text{5} & \quad + \quad \text{SbF}_6^- \\
\end{align*}
\]

X-ray analyses of \textbf{4} and \textbf{5} have been performed (Figure 3). The M–P, M–Cl(1) and M–Cl(2) (M = Ru or Rh) parameters for \textbf{4} and \textbf{5} are similar to those of analogous complexes with PTA.\textsuperscript{2b,4h,4j} Moreover, upon coordination of the phosphine \textbf{2a}, there are minimal differences in the P–C and P–C–N metric parameters with respect to \textbf{1b}, \textbf{2b} or \textbf{3a}. As seen previously for \textbf{1b}, \textbf{2b} or \textbf{3a}, pairs of intramolecular N–H···N hydrogen-bonds are once again maintained upon complexation [\textbf{4}, N(1)···N(2) 2.894(3) Å, H(1A)···N(2) 2.22(3) Å, N(1)–H(1A)···N(2) 130(3)° and N(1)···N(3) 2.840(3) Å, H(1B)···N(3) 2.24(3) Å, N(1)–H(1B)···N(3) 128(3)°; \textbf{5}, N(1)···N(2) 2.952(9) Å, H(1A)···N(2) 2.34 Å, N(1)–H(1A)···N(2) 124° and N(1)···N(3) 2.851(8) Å, H(1B)···N(3) 2.18 Å, N(1)–H(1B)···N(3) 129°]. Additional weak H-bonding interactions link molecules into dimer pairs (Supporting Information) and is a feature that has recently been observed in cationic dimeric \( \text{Ru}^{\text{II}} \) complexes of PTA.\textsuperscript{22}
Figure 3. (a) ORTEP of the cation in 4. Selected bond lengths (Å) and angles (deg). Ru(1)−Cl(1) 2.4064(7), Ru(1)−Cl(2) 2.4103(6), Ru(1)−P(1) 2.3293(6), Ru(1)−Cav 2.210(3), P(1)−C(1) 1.843(2), P(1)−C(9) 1.831(3), P(1)−C(10) 1.828(2). Cl(1)−Ru(1)−Cl(2) 88.00(2), Cl(1)−Ru(1)−P(1) 87.60(2), Cl(2)−Ru(1)−P(1) 83.75(2), P(1)−C(1)−N(1) 115.07(16), P(1)−C(9)−N(2) 110.35(16), P(1)−C(10)−N(3) 111.74(16). (b) ORTEP of the cation in 5. Selected bond lengths (Å) and angles (deg). Rh(1)−Cl(1) 2.406(2), Rh(1)−Cl(2) 2.424(2), Rh(1)−P(1) 2.2851(19), Rh(1)−Cav 2.188(8), P(1)−C(1) 1.834(7), P(1)−C(9) 1.836(8), P(1)−C(10) 1.830(7). Cl(1)−Rh(1)−Cl(2) 92.67(8), Cl(1)−Rh(1)−P(1) 88.85(7), Cl(2)−Rh(1)−P(1) 83.37(7), P(1)−C(1)−N(1) 115.4(5), P(1)−C(9)−N(2) 110.1(5), P(1)−C(10)−N(3) 110.0(5).

The electronic properties of 1a and 1b have been evaluated through preparation of the square-planar dicationic Rh¹ carbonyl complexes 6a (88%) and 6b (93%) from Rh₂(CO)₄(µ-Cl)₂ and the appropriate ligand. Both Rh¹ compounds displayed poor solubility in common solvents preventing full
characterization. However FT-IR spectra of 6a and 6b were recorded as KBr pellets and showed, in each case, a single terminal carbonyl band at \( \nu_{\text{CO}} \) 1979 cm\(^{-1}\). These findings suggest the electronic properties of 1a (R = CH\(_2\)C\(_6\)H\(_5\)) and 1b (R = 4-CH\(_2\)C\(_6\)H\(_4\)F) are similar despite the different \textit{para} substituents. Although no direct comparisons between the FT-IR data for 6a/6b with the known neutral complexes \textit{trans}-RhCl(CO)(L)\(_2\) [L = PTA, \( \nu_{\text{CO}} \) 1963 cm\(^{-1}\) (chloroform); L = “lower-rim” trisubstituted analogues of PTA, \( \nu_{\text{CO}} \) 1978–1987 cm\(^{-1}\) (chloroform)]\(^{2c,23}\) can be drawn, 1a and 1b can be viewed as possessing similar electron donating properties to this series of PTA ligands.

**Concluding Remarks**

In summary, we have shown how simple modification of the PTA core can be achieved in which non covalent interactions maintain the rigid cage structure in the solid state. Further studies are in progress and directed towards understanding the properties of this ligand family in aqueous and organic media, their coordination chemistry and potential catalytic/medicinal applications.
Acknowledgements

We thank the EPSRC, Loughborough University and Niger Delta University, Bayelsa State, Nigeria for funding (ATE, AJL). Rhodia UK Ltd (Dr Ranbir Padda) and Johnson Matthey are gratefully acknowledged for their kind donations of THPC and precious metal salts, respectively. We wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury.

Supporting Information Available

X-ray data for 1b, 2b, 3a, 4·1.67CH₂Cl₂ and 5·2CH₂Cl₂ in CIF format. This material is available free of charge via the internet at http://pubs.acs.org.

References


Table of Contents Synopsis – New intramolecular N–H···N stabilized cage phosphines and their selected complexes with Ru$^{II}$, Rh$^{I}$ and Rh$^{III}$ have been synthesized and fully characterized. Comparisons with 1,3,5-triaza-7-phosphaadamantane (PTA) and its complexes revealed similar steric and electronic properties.

$$\text{R} = \text{C}_6\text{H}_5\text{CH}_2, 4\text{-FC}_6\text{H}_4\text{CH}_2$$
$$\text{X} = \text{Cl}, \text{SbF}_6, \text{PF}_6$$