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Synthesis, characterization and solubility studies of four new highly water soluble 1,3,5-triaza-7-phosphaadamantane (PTA) salts and their gold(I) complexes

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ABSTRACT

The synthesis of new water soluble *N*-alkylated derivatives of 1,3,5-triaza-7-phosphaadamantane is presented. The compounds were characterized by means of NMR and IR spectroscopy, mass spectrometry, high resolution mass spectrometry, elemental analysis and X-ray diffraction analysis. The water solubility of these compounds was found to be up to an astonishing 1450 g/L. Several different reactions were performed utilizing these highly interesting compounds as starting materials. It was shown that the substitution of the counter ion can be performed easily. Also transformations at the PTA framework were possible, as shown by an ester cleavage example. To prove that the resulting PTA derivatives are competent as ligands for transition metals, gold(I) complexes were synthesized, using Au(tht)Cl as the metal source. The resulting gold(I) complexes were characterized by ^{1}H NMR and IR spectroscopy, mass and high resolution mass spectrometry or elemental analysis.

1. Introduction

Since the early days of classical chemistry, water has been a common solvent and ligand in many organic and inorganic reactions. As chemistry evolved, new reactions, transformations, complexes and ligands were discovered that required completely anhydrous conditions as well as special techniques to keep water out of the reaction [1]. These new methods provided access to a plethora of new, innovative reactions and transformations and have enlarged the line-up of accessible compounds considerably.

In recent years, water has been experiencing a renaissance as a reaction medium. It was found that the aqueous medium can enhance known (catalytic) reactions and transformations dramatically [2–4]. To utilize known and to discover new advantages of water as a reaction medium comprehensively, new water soluble and water stable transition metal complexes need to be provided. One of the most commonly applied phosphane ligands in the synthesis of water soluble transition metal complexes is the monodentate cage-like 1,3,5-triaza-7-phosphaadamantane (PTA) **1** and its monoalkylated ammonia salt derivatives (**2**) [5]. The advantage of this unique class of ligands is their inherently high water solubility (236 g/L for PTA) [6] and their low sensitivity towards oxidation [7] (Scheme 1).

PTA was first reported in 1974 by Daigle et al. [8]. Although the coordination chemistry of many different transition metal complexes with PTA as a ligand have been studied in details [5,9–15], surprisingly the preparation and application of the corresponding PTA ammonia salts have experienced only little attention over a long period of time. In the first publication documenting the synthesis of PTA it was already pointed out that PTA reacts readily with alkyl halogenides to afford *N*-alkylated quarternary ammonia salts [8]. In order to increase the water solubility of PTA derivatives and the corresponding transition metal complexes, the issue of providing new variously substituted *N*-alkylated PTA derivatives was resumed to establish the grounds for new synthetic routes in the modification of the adamantanoid framework. So far PTA has been derivatized to some differently *N*-monoalkylated ammonia salts. The most commonly compounds found were synthesized by reacting PTA with benzylchloride [16], MeI [17,18], EtI [19], ^{n}PrI [20], ^{n}BuI [21], $I(CH_2)_4I$ [22], $MeOSO_2CF_3$ [23] and $C_5H_4NCH_2Br$ [24] to furnish the mono-*N*-alkylated compounds.

In the recent past PTA and its derivatives have found their way into catalysis [21,25], underlining the importance of this class of compounds.

Besides a rich coordination chemistry of many transition metals [5,15,21,26], only a few gold complexes using PTA salts as ligands

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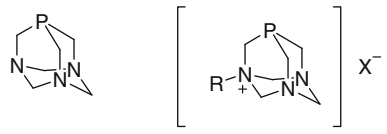


Scheme 1. PTA **1** and *N*-monosubstituted derivatives **2**.

have been reported so far [19,20,27–29]. Herein we present new routes and transformations to gain access to new *N*-alkylated PTA derivates and their application as ligands for gold(I) complexes. The water solubility of the newly synthesized PTA derivatives and their gold(I) complexes were investigated as well.

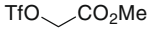
2. Experimental

2.1. General methods, materials and measurements

NMR spectra were recorded on Bruker ARX 300, ARX 400, ARX 500 and ARX 600 spectrometers. ^{1}H NMR spectra were measured at 300, 400, 500 and 600 MHz; ^{13}C{1H} NMR spectra were recorded at 101 and 126 MHz. Chemical shifts are quoted relative to residual solvent peaks. ^{31}P{1H} NMR spectra were measured at 203 and 162 MHz. Chemical shifts are quoted relative to an external H_3PO_4 standard. ^{19}F{1H} NMR spectra were collected at 176 MHz with chemical shifts quoted to an external $CFCl_3$ standard. Coupling constants, *J*, are given in Hz. Multiplicity as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad signal. Proton- and carbon-assignment was achieved using H,H and C,H correlation spectra, and HMBC spectra. Mass spectra were measured on a MALDI-TOF Microflex [Laser N_2 (337 nm 3.57 eV); Matrix: DHB or DIT], Finnigan MAT 90, Bruker Daltonics micrOTOF-Q, Varian 711 and Bruker Daltonics FLEX-PC. IR spectra were recorded on Perkin–Elmer 100 and Bruker Vector 22 spectrometers. Elemental analyses were obtained by using a Perkin–Elmer 240 B, Perkin–Elmer 2400 B and Carlo Erba Strumentazione Elemental Analyser 1106. Melting points were measured on a Fisher-Johns Melting Point Apparatus Kofler and Büchi SMP 20 and are uncorrected. Chemicals were purchased from Aldrich, Lancaster and Fluka and were used without further purification. Diethylether (Et_2O) and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled prior to use. Acetone and dichloromethane (DCM) were dried over CaH_2 and distilled prior to use. Dry methanol (MeOH) was purchased from Fluka and used without further purification. The reactions requiring the exclusion of air were carried out under an atmosphere of argon or nitrogen in oven dried glassware using standard Schlenk techniques.

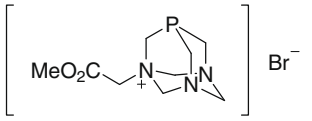
2.2. Synthesis of the compounds

2.2.1. (methoxycarbonyl)methyltrifluoromethane sulfonate [30] (**6**)



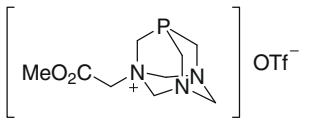
Under an atmosphere of argon, using standard Schlenk techniques, trifluoromethanesulfonic anhydride (1.44 g, 5.10 mmol) was added dropwise to a mixture of methyl glycolate (**7**) (400 mg, 4.44 mmol) and pyridine (456 mg, 5.78 mmol) in DCM (8 mL) at −78 °C. After the addition was complete, the mixture was stirred for an additional 35 min at −78 °C. The reaction mixture was then allowed to warm up to room temperature and stirred for further 3 h. The reaction was quenched by adding water (10 mL) and DCM (10 mL). The aqueous phase was extracted two times with DCM. After evaporation of the solvent, **6** was obtained as a colorless oil (957 mg, 4.31 mmol, 97%). IR (neat): $\tilde{\nu}$ = 1765, 1411, 1200, 1138, 1028, 810, 610, 494, 238 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.86 (s, 3H, COO*Me*), 4.92 (s, 2H, TfO*CH*$_2$COOMe) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 53.2 (COO*Me*), 68.8 (TfO*CH*$_2$-COOMe), 118.4 ($J_{F,C}$ = 319.5 Hz, *CF*$_3$), 164.9 (COOMe). ^{19}F NMR (176 MHz, $CDCl_3$, 25 °C): δ = −74.61 ppm. MALDI− MS: *m/z* = 149 [TfO]$^-$. MS: (EI+, 70 eV): *m/z* = 221 (1) [M−H]$^+$, 99 (18), 79 (51), 69 (100), 59 (51). *Anal.* Calc. $C_4H_5F_3O_5S$ (222.1): C, 21.63; H, 2.27. Found: C, 21.11; H, 2.66%. HRMS: (CI+, reaction gas: CH_4): Calc. for $C_4H_6F_3O_5S$: 222.9883. Found: 222.9864.

2.2.2. 1-Methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane bromide [PTACH$_2$CO$_2$Me]Br (***8***)



Under an atmosphere of argon, using standard Schlenk techniques, methyl bromoacetate (76.5 mg, 500 μmol) in acetone (10 mL) was added dropwise to a mixture of PTA (78.6 mg, 500 μmol) in acetone (10 mL) at 0 °C. After the addition was complete, the mixture was stirred for an additional 25 min at 0 °C. The reaction mixture was then allowed to warm up to room temperature and Et_2O (10 mL) was added to complete precipitation. After filtration, washing with Et_2O and drying *in vacuo*, **8** was obtained as a colorless solid (147 mg, 472 μmol, 94%). M.p.: 148–150 °C. IR (neat): $\tilde{\nu}$ = 2907, 1742, 1451, 1220, 1029, 983, 909, 807, 757, 742, 552, 439, 395, 353, 258 cm^{-1}. ^{1}H NMR (500 MHz, [D$_4$] methanol, 25 °C): δ = 3.35 (s, 3H, COO*Me*), 3.86 (s, 2H, N$^+$*CH*$_2$COOMe), 3.94–4.08 (m, 4H, N*CH*$_2$P), 4.53 (dt, $J_{H,H}$ = 13.6 Hz, 1.7 Hz, 1H, N*CH*$_{2a}$N), 4.64–4.69 (m, 3H, N*CH*$_{2b}$N, N$^+$*CH*$_2$P), 5.05 (d, $J_{H,H}$ = 11.1 Hz, 2H, N$^+$*CH*$_{2a}$N), 5.31–5.39 (m, 2H, N$^+$*CH*$_{2b}$N), ppm. ^{13}C NMR (126 MHz, [D$_4$] methanol, 25 °C): δ = 47.7 ($J_{P,C}$ = 21.2 Hz, 2C, N*CH*$_2$P), 50.0 (N$^+$CH$_2$COO*Me*), 53.9 (N$^+$*CH*$_2$COOMe), 55.4 ($J_{P,C}$ = 35.0 Hz, N$^+$*CH*$_2$P), 71.5 (N*CH*$_2$N), 82.3 (2C, N$^+$*CH*$_2$N), 166.1 (*C*OOMe) ppm. ^{31}P{1H} NMR (162 MHz, [D$_4$] methanol, 25 °C): δ = −82.33 ppm. MALDI+ MS: *m/z* = 230 [M]$^+$, 187 [M−C$_2$H$_5$N]$^+$, 129 [M−C$_4$H$_7$NO$_2$]$^+$. ESI+ MS: *m/z* (%): 230 (12) [M]$^+$, 218 (51), 189 (15), 175 (100), 158 (7), 146 (68), 129 [M−C$_4$H$_7$NO$_2$]$^+$ (9), 117 (6). *Anal.* Calc. for $C_9H_{17}BrN_3O_2P$ (310.1): C, 34.86; H, 5.53; N, 13.55. Found: C, 34.23; H, 5.56; N, 13.33%. HRMS (ESI+): Calc. for $C_9H_{17}N_3O_2P$: 230.1053. Found: 230.1040.

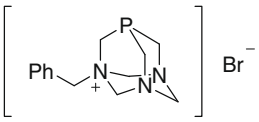
2.2.3. 1-Methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane triflate [PTACH$_2$CO$_2$Me]OTf (***9***)



Under an atmosphere of argon, using standard Schlenk techniques, (methoxycarbonyl)methyltrifluoromethane sulfonate (111 mg, 500 μmol) in acetone (10 mL) was added dropwise to a mixture of PTA (78.6 mg, 500 μmol) in acetone (10 mL) at 0 °C. After the addition was complete, the mixture was stirred for an additional 35 min at 0 °C. The reaction mixture was then allowed to warm up to room temperature and Et_2O (10 mL) was added to complete precipitation. After filtration, washing with Et_2O and drying *in vacuo*, **9** was obtained as a colorless solid (165 mg, 435 μmol, 87%). After recrystallization from

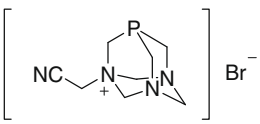
water, single crystals suitable X-ray diffraction were obtained. M.p.: 119–121 °C. IR (neat): $\tilde{\nu}$ = 2963, 1760, 1457, 1254, 1213, 1154, 1025, 907, 804, 754, 572, 517, 347, 253 cm^{-1}. ^1H NMR (400 MHz, [D_6] acetone, 25 °C): δ = 3.82 (s, 3H, COO*Me*), 4.11 (s, 2H, N^+CH_2COOMe), 4.12 (d, $J_{P,H}$ = 10.5 Hz, 4H, NCH_2P), 4.63 (d, $J_{H,H}$ = 13.6 Hz, 1H, $NCH_{2a}N$), 4.74 (dt, $J_{H,H}$ = 13.5 Hz, 1.7 Hz, 1H, $NCH_{2b}N$), 4.84 (d, $J_{P,H}$ = 6.0 Hz, 2H, N^+CH_2P), 5.28 (d, $J_{H,H}$ = 11.5 Hz, 2H, $N^+CH_{2a}N$), 5.49–5.57 (m, 2H, $N^+CH_{2b}N$) ppm. ^{13}C NMR (125.8 MHz, [D_4] methanol, 25 °C): δ = 47.7 ($J_{P,C}$ = 21.2 Hz, 2C, NCH_2P), 50.1 (N^+CH_2COO*Me*), 53.9 (N^+CH_2COOMe), 55.4 ($J_{P,C}$ = 34.9 Hz, N^+CH_2P), 71.5 (NCH_2N), 82.4 (2C, N^+CH_2N), 122.0 ($J_{F,C}$ = 318.2 Hz, CF_3), 166.1 (COOMe) ppm. $^{31}P\{1H\}$ NMR (162 MHz, [D_6] acetone, 25 °C): δ = −82.14 ppm. ^{19}F NMR (176 MHz, [D_6] acetone, 25 °C): δ = −80.29 ppm. MALDI+ MS: *m/z* = 230 $[M]^+$, 187 $[M-C_2H_5N]^+$, 129 $[M-C_4H_7NO_2]^+$. MALDI− MS: *m/z* = 149 $[M]^-$. ESI+ MS: *m/z* = 230 (100) $[M]^+$, 187 (90) $[M-C_2H_5N]^+$, 175 (14), 146 (10), 129 $[M-C_4H_7NO_2]^+$, 100 (6). *Anal.* Calc. for $C_{10}H_{17}F_3N_3O_5PS$ (379.3): C, 31.67; H, 4.52; N, 11.08. Found: C, 31.28; H, 4.57; N, 10.76%. HRMS (ESI+): Calc. for $C_9H_{17}N_3O_2P$: 230.1053. Found: 230.1046.

2.2.4. 1-Benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane bromide [PTAbenzyl]Br (**10**)



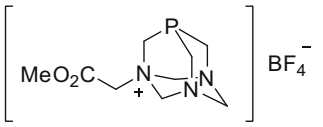
Under an atmosphere of argon, using standard Schlenk techniques, benzyl bromide (85.5 mg, 500 μmol) in acetone (10 mL) was added dropwise to a mixture of PTA (78.6 mg, 500 μmol) in acetone (10 mL) at 0 °C. After the addition was complete, the mixture was stirred for an additional 25 min at 0 °C. The reaction mixture was then allowed to warm up to room temperature and Et_2O (10 mL) was added to complete precipitation. After filtration, washing with Et_2O and drying *in vacuo,* **10** was obtained as a colorless solid (146 mg, 445 μmol, 89%). Decomp. p.: 170 °C. IR (neat): $\tilde{\nu}$ = 2907, 1454, 1312, 1216, 1126, 1066, 1032, 976, 895, 803, 756, 730, 701, 554, 439, 396, 246 cm^{-1}. ^1H NMR (400 MHz, [D_4] methanol, 25 °C): δ = 3.79–3.89 (m, 2H, NCH_2P), 3.91–4.01 (m, 2H, NCH_2P), 4.15 (s, 2H, N^+CH_2Ph), 4.27 (d, $J_{P,H}$ = 6.5 Hz, 2H, N^+CH_2P), 4.46 (dt, $J_{H,H}$ = 13.6 Hz, 1.7 Hz, 1H, $NCH_{2a}N$), 4.64 (dt, $J_{H,H}$ = 13.6 Hz, 1.9 Hz, 1H, $NCH_{2b}N$), 4.95 (d, $J_{H,H}$ = 11.7 Hz, 2H, $N^+CH_{2a}N$), 5.03 (d, $J_{H,H}$ = 11.2 Hz, 2H, $N^+CH_{2b}N$), 7.52–7.60 (m, 5H, Ph*H*) ppm. ^{13}C NMR (101 MHz, [D_4] methanol, 25 °C): δ = 47.5 ($J_{P,C}$ = 21.2 Hz, 2C, NCH_2P), 54.1 ($J_{P,C}$ = 34.5 Hz, N^+CH_2P), 67.2 (N^+CH_2Ph), 71.4 (NCH_2N), 81.0 (2C, N^+CH_2N), 126.7 (Ph*C*), 130.5 (2C, Ph*C*), 131.9 (Ph*C*), 134.1 (2C, Ph*C*) ppm. $^{31}P\{1H\}$ NMR (162 MHz, [D_4] methanol, 25 °C): δ = −81.48 ppm. ESI+ MS: *m/z* (%): 248 (100) $[M]^+$, 230 (17), 205 (17) $[M-CH_4N_2]^+$, 187 (18), 134 (45), 129 (17) $[M-C_8H_9N]^+$. *Anal.* Calc. for $C_{13}H_{19}BrN_3P$ (327.1): C, 47.58; H, 5.84; N, 12.80. Found: C, 47.18; H, 5.67; N, 12.76%. HRMS (ESI+): Calc. for $C_{13}H_{19}N_3P$: 248.1311. Found: 248.1306.

2.2.5. 1-Cyanomethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane bromide [PTACH$_2$CN]Br (**11**)



Under an atmosphere of argon, using standard Schlenk techniques, bromoacetonitrile (120 mg, 1.0 mmol) in acetone (10 mL) was added dropwise to a mixture of PTA (157 mg, 1.0 mmol) in acetone (10 mL) at −45 °C over a period of 1.5 h. After the addition was complete, the mixture was stirred for an additional 1.5 h at −45 °C. The reaction mixture was then allowed to warm up to room temperature and Et_2O (10 mL) was added to complete precipitation. After filtration, washing with Et_2O and drying *in vacuo,* **11** was obtained as a colorless solid (224 mg, 810 μmol, 81%). Decomp. p.: 165 °C. IR (neat): $\tilde{\nu}$ = 2962, 2871, 1414, 1313, 1224, 1125, 1090, 1027, 984, 957, 913, 904, 803, 750, 731, 545, 396, 378, 305 cm^{-1}. ^1H NMR (400 MHz, [D_4] methanol, 25 °C): δ = 3.85–4.10 (m, 6H, NCH_2P, N^+CH_2CN), 4.52 (dt, $J_{H,H}$ = 13.7 Hz, 1.9 Hz, 1H, $NCH_{2a}N$), 4.58–4.64 (m, 2H, N^+CH_2P), 4.68 (dt, $J_{H,H}$ = 13.8 Hz, 1.9 Hz, 1H, $NCH_{2b}N$), 5.12 (d, $J_{H,H}$ = 10.9 Hz, 2H, $N^+CH_{2a}N$), 5.21–5.27 (m, 2H, $N^+CH_{2b}N$) ppm. $^{31}P\{1H\}$ NMR (162 MHz, [D_4] methanol, 25 °C): δ = −80.74 ppm. MALDI+ MS: *m/z* = 197 $[M]^+$. ESI+ MS: *m/z* = 197 (100) $[M]^+$, 185 (11), 175 (13), 159 (12), 154 (62) $[M-C_2H_5N]^+$, 142 (36) $[M-C_2H_3N_2]^+$, 113 (9). HRMS (ESI+): Calc. for $C_8H_{14}N_4P$: 197.0951. Found: 197.0952.

2.2.6. 1-Methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane tetrafluoroborate [PTACH$_2$CO$_2$Me]BF$_4^-$ (12)



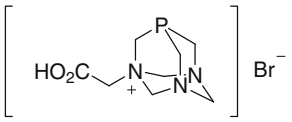
Under an atmosphere of argon, using standard Schlenk techniques, methylbromoacetate (153 mg, 1.0 mmol) in acetone (5 mL) and MeOH (5 mL) was added dropwise to a mixture of PTA (157 mg, 1.0 mmol) and $NaBF_4$ (110 mg, 1.0 mmol) in acetone (5 mL) and MeOH (5 mL) at 0 °C. After the addition was complete, the mixture was stirred for an additional 25 min at 0 °C. The reaction mixture was then allowed to warm up to room temperature. After filtration, washing with Et_2O and drying *in vacuo,* **12** was obtained as a colorless solid (32.0 mg, 10.1 μmol, 10%).

2.3. Alternative preparation

Under an atmosphere of nitrogen, using standard Schlenk techniques, **8** (24.4 mg, 78.9 μmol) and $NaBF_4$ (8.68 mg, 78.9 μmol) were dissolved in MeOH (1.75 mL) and acetone (2.5 mL). The mixture was heated to 40 °C for 2 h, cooled to 0 °C, carefully concentrated under reduced pressure and stored at −28 °C over night. The formed colorless precipitate was filtered off. The remaining solvent in the filtrate was removed under reduced pressure. Drying *in vacuo* yielded **12** as a colorless solid (11.2 mg, 35.3 μmol, 45%).

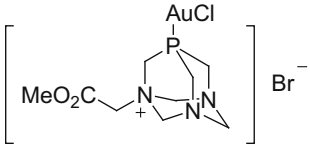
M.p.: 137–139 °C. IR (neat): $\tilde{\nu}$ = 2950, 1745, 1453, 1429, 1224, 1051, 1028, 980, 910, 805, 739, 552, 520, 441, 349, 242, 233 cm^{-1}. ^1H NMR (400 MHz, [D_4] methanol, 25 °C): δ = 3.35 (s, 3H, COO*Me*) 3.85 (s, 2H, N^+CH_2COOMe), 3.85–4.10 (m, 4H, NCH_2P), 4.51 (dt, $J_{H,H}$ = 13.7 Hz, 1.7 Hz, 1H, $NCH_{2a}N$), 4.63 (d, $J_{P,H}$ = 5.4 Hz, 2H, N^+CH_2P), 4.66 (dt, $J_{H,H}$ = 13.7 Hz, 1.7 Hz, 1H, $NCH_{2b}N$), 5.03 (d, $J_{H,H}$ = 10.9 Hz, 2H, $N^+CH_{2a}N$), 5.29–5.36 (m, 2H, $N^+CH_{2b}N$) ppm. $^{31}P\{1H\}$ NMR (162 MHz, [D_4] methanol, 25 °C): δ = −82.37 ppm. ^{19}F NMR (176 MHz, [D_4] methanol, 25 °C): δ = −154.07 ppm. MALDI+ MS: *m/z* = 230 $[M]^+$, 187 $[M-C_2H_5N]^+$, 129 $[M-C_4H_7NO_2]^+$. MALDI− MS: *m/z* = 87 $[M]^-$. ESI+ MS: *m/z* = 230 (100) $[M]^+$, 187 (91) $[M-C_2H_5N]^+$, 175 (8), 129 (15) $[M-C_4H_7NO_2]^+$, 116 (6), 100 (6). *Anal.* Calc. for $C_9H_{17}F_4BN_3O_2P$ (317.0): C, 34.10; H, 5.40; N, 13.25. Found: C, 34.12; H, 5.41; N, 12.83%. HRMS (ESI+): Calc. for $C_9H_{17}N_3O_2P$: 230.1053. Found: 230.1044.

*2.3.1. 1-Carboxymethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane bromide [PTACH$_2$CO$_2$H]Br (**13**)*



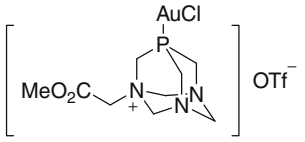
Under an atmosphere of argon, using standard Schlenk techniques, **8** (100 mg, 322 μmol) was added to a mixture of NaOH (12.9 mg, 322 μmol) in Et$_2$O (20 mL) at room temperature. The mixture was stirred for 3 days at room temperature. After filtration, washing with Et$_2$O and drying *in vacuo,* **13** was obtained as a colorless solid (84.1 mg, 154 μmol, 48%). Decomp. p.: 190 °C. IR (neat): $\tilde{\nu}$ = 3430, 2944, 1609, 1439, 1397, 1221, 1154, 981, 904, 811, 752, 687, 553, 499, 436, 396, 263, 258, 245, 238 cm^{-1}. ^{1}H NMR (400 MHz, D$_2$O, 25 °C): δ = 3.52 (s, 2H, *CH*$_2$COOH), 3.85–4.09 (m, 4H, NC*H*$_2$P,), 4.47 (dt, $J_{H,H}$ = 13.6 Hz, 1.9 Hz, 1H, NC*H*$_{2a}$N), 4.58–4.64 (m, 3H, NC*H*$_{2b}$N, N$^+$C*H*$_2$P), 4.94 (d, $J_{H,H}$ = 11.2 Hz, 2H, N$^+$C*H*$_{2a}$N), 5.20–5.38 (m, 2H, N$^+$C*H*$_{2b}$N) ppm. (s, 1H, CHCOO*H*) was not detected, possibly being under the water signal at 4.79 ppm. ^{31}P{1H} NMR (162 MHz, [D$_4$] methanol, 25 °C): δ = −84.04 ppm. ESI+ MS: *m/z* = 238 (100) [M−H+Na]$^+$, 195 (9), 175 (7), 146 (5), 124 (8). HRMS (ESI+): Calc. for C$_8$H$_{14}$N$_3$NaO$_2$P: 238.0716. Found: 238.0707.

*2.3.2. (1-Methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane-P)gold(I) bromide chloride [AuCl(PTACH$_2$CO$_2$Me)]Br (**15**)*



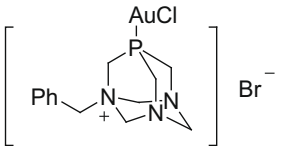
Compound **8** (50.0 mg, 161 μmol) was added to a mixture of AuCl(tht) (**14**) (51.7 mg, 161 μmol) in acetone (4 mL) at room temperature. The mixture was stirred for 2 days at room temperature. After addition of Et$_2$O (5 mL), filtration, washing with Et$_2$O and drying *in vacuo* **15** was obtained as a slightly orange solid (74.1 mg, 137 μmol, 85%). Decomp. p.: 170 °C. IR (neat): $\tilde{\nu}$ = 3368, 2954, 2914, 2498, 2158, 2025, 1976, 1746, 1449, 1309, 1216, 1097, 1029, 985, 901, 808, 737, 544, 436, 388, 354, 315, 279 cm^{-1}. ^{1}H NMR (400 MHz, [D$_4$] methanol, 25 °C): δ = 3.89 (s, 3H, COO*Me*), 4.15 (d, $J_{H,H}$ = 2.0 Hz, 2H, N$^+$C*H*$_2$COOMe), 4.44–4.62 (m, 5H, NC*H*$_2$P, NC*H*$_{2a}$N), 4.72 (d, $J_{H,H}$ = 13.6 Hz, 1H, NC*H*$_{2b}$N), 5.10–5.18 (m, 4H, N$^+$C*H*$_2$P, N$^+$C*H*$_{2a}$N), 5.53 (d, $J_{H,H}$ = 11.5 Hz, 2H, N$^+$C*H*$_{2b}$N) ppm. ^{31}P{1H} NMR (162 MHz, [D$_4$] methanol, 25 °C): δ = −31.04 ppm. ESI+ MS: *m/z* = 707 (3), 631 (25), 594 (85), 592 (14), 562 (92), 560 (100), 518 (80), 516 (32), 505 (11) [M+Br]$^+$, 496 (30), 494 (20), 462 (3) [M+Cl]$^+$, 414 (16), 371 (7). *Anal.* Calc. for C$_9$H$_{17}$AuBrClN$_3$O$_2$P (542.6): C, 19.92; H, 3.16; N, 7.74. Found: C, 19.48; H, 3.50; N, 7.39%.

*2.3.3. (1-Methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane-P)gold(I) chloride triflate [AuCl(PTACH$_2$CO$_2$Me)]OTf (**16**)*



Compound **9** (42.3 mg, 132 μmol) was added to a mixture of AuCl(tht) (50.0 mg, 132 μmol) in acetone (4 mL) at room temperature. The mixture was stirred for 8 h at room temperature. After addition of Et$_2$O (5 mL), filtration, washing with Et$_2$O and drying *in vacuo,* **16** was obtained as a colorless solid (60.9 mg, 99.6 μmol, 76%). Decomp. p.: 145 °C. IR (neat): $\tilde{\nu}$ = 3490, 2986, 1745, 1453, 1246, 1223, 1160, 1026, 985, 808, 735, 635, 574, 516, 318, 246 cm^{-1}. ^{1}H NMR (400 MHz, [D$_4$] methanol, 25 °C): δ = 3.88 (s, 3H, COO*Me*), 4.07 (d, $J_{H,H}$ = 2.1 Hz, 2H, N$^+$C*H*$_2$COOMe), 4.35–4.55 (m, 5H, NC*H*$_2$P, NC*H*$_{2a}$N), 4.70 (d, $J_{H,H}$ = 13.9 Hz, 1H, NC*H*$_{2b}$N), 5.02 (d, $J_{P,H}$ = 5.6 Hz, 2H, N$^+$C*H*$_2$P), 5.10 (d, $J_{H,H}$ = 11.6 Hz, 2H, N$^+$C*H*$_{2a}$N), 5.47 (d, $J_{H,H}$ = 10.9 Hz, 2H, N$^+$C*H*$_{2b}$N) ppm. ^{31}P{1H} NMR (162 MHz, [D$_4$] methanol, 25 °C): δ = −31.58 ppm. ^{19}F NMR (176 MHz, [D$_4$] methanol, 25 °C): δ = −80.35 ppm. ESI+ MS: *m/z* = 863 (43), 689 (11), 675 (6) [M+2Na+TfO+Cl+H$_2$O]$^+$, 631 (100), 530 (8), 501 (21), 462 (5) [M+Cl]$^+$, 407 (2). *Anal.* Calc. for C$_{10}$H$_{17}$AuClF$_3$N$_3$O$_6$PS (611.7): C, 19.63; H, 2.80; N, 6.87. Found: C, 19.26; H, 3.00; N, 6.60%. HRMS (ESI+): Calc. for C$_9$H$_{17}$AuClN$_3$O$_2$P: 462.0407. Found: 462.0383.

*2.3.4. (1-Benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane-P)gold(I) bromide chloride [AuCl(PTAbenzyl)]Br (**17**)*



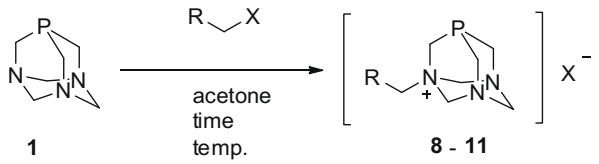
Compound **10** (150 mg, 457 μmol) was added to a mixture of AuCl(tht) (147 mg, 457 μmol) in acetone (15 mL) at room temperature. The mixture was stirred for 14 h at room temperature. After addition of Et$_2$O (5 mL), filtration, washing with Et$_2$O and drying *in vacuo,* **17** was obtained as a colorless solid (178 mg, 318 μmol, 70%). Decomp. p.: 145 °C. IR (neat): $\tilde{\nu}$ = 2960, 1454, 1308, 1121, 1031, 988, 924, 897, 816, 757, 731, 701, 580 cm^{-1}. ^{1}H NMR (600 MHz, [D$_6$] DMSO, 25 °C): δ = 4.10–4.18 (d, $J_{H,H}$ = 14.8 Hz, 2H, NC*H*$_2$P), 4.21–4.31 (m, 4H, NC*H*$_2$P, N$^+$C*H*$_2$Ph), 4.34 (d, $J_{H,H}$ = 13.7 Hz, 1H, N$^+$C*H*$_{2a}$P), 4.52–4.64 (m, 3H, NC*H*$_2$N, N$^+$C*H*$_{2b}$P), 4.98 (bs, 2H, N$^+$C*H*$_{2a}$N), 5.18 (bs, 2H, N$^+$C*H*$_{2b}$N), 7.51–7.61 (m, 5H, Ph*H*) ppm. ^{31}P{1H} NMR (202.5 MHz, [D$_4$] methanol, 25 °C): δ = −31.54 ppm. ESI+ MS: *m/z* (%): 375 (51), 360 (63) [M−C$_9$H$_{11}$]$^+$, 334 (100), 318 (24). HRMS (ESI): Calc. for C$_4$H$_7$AuClN$_3$P: 360.9804. Found: 360.9794.

3. Results and discussions

3.1. Synthesis of N-alkylated PTA salts

The synthesis of the quarternary *N*-alkylated-PTA compounds was carried out starting from a suspension of PTA in acetone to which benzylbromide (**3**), methyl bromoacetate (**4**), bromoacetonitrile (**5**) or (methoxycarbonyl)methyltrifluoromethane sulfonate (**6**), each dissolved in acetone, was added. Compound **6** was synthesized from the commercially available methyl glycolate (**7**) according to a literature procedure [30]. The reactions were carried out at 0 °C and −45 °C, respectively. After an appropriate reaction time, the desired monoalkylated ammonia salts were obtained as colorless solids *via* precipitation triggered by the addition of a suitable amount of diethyl ether. No multiple alkylation was observed. A polyalkylated PTA salt was not observed, even after refluxing in acetone with 8 equivalents of bromide or triflate. It has been reported that triflate containing alkylating reagents are able to open the PTA cage [31]. Using 2 equivalents of **6**, even at elevated tem-

peratures, compound **9** was observed exclusively. In the case of 8 equivalents in refluxing acetone, decomposition of the starting material was observed.



The desired compounds **8**–**11** were isolated in good to excellent reproducible yields after short reaction times, with high purity confirmed by ^{1}H and ^{31}P NMR spectroscopy, and including elemental analysis for compounds **8**, **9** and **10**. No further purification of the reaction products was necessary (Table 1). Due to the higher reactivity of the nitrile compound **5**, the reaction had to be carried out at −45 °C. Performing the reaction at 0 °C resulted in the yield and purity of the isolated product to be significantly lower (Table 1, entry 4). The obtained products were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR spectroscopy, mass spectrometry and elemental analysis, and also X-ray diffraction analysis for **9**. Signals of the methylene moieties between a quarternary and tertiary nitrogen were detected to be in the range δ = 4.90–5.40 ppm (in [D_4] methanol; **8**, **10**), at δ = 5.28 and δ = 5.52 ppm (in [D_6] acetone; **9**) and at δ = 5.12 and δ = 5.25 ppm (in [D_4] methanol; **11**). At δ = 3.86 (**8**, [D_4] methanol) and at δ = 4.11 (**9**, [D_6] acetone) ppm, the methylene moiety adjacent to the quarternary nitrogen and the ester group was detected. The proton chemical shift of the methyl ester group was detected at δ = 3.35 ppm for **8** in [D_4] methanol while δ = 3.82 ppm was found for **9** in [D_6] acetone. As the anion should not have a larger effect on the chemical shift, the observed difference seems to be dependant on solvent effects; it is plausible that methanol is capable of interacting more strongly with the ester group *via* hydrogen bonds. The proton signals of the benzylic moiety of compound **10** were detected at δ = 4.15 ppm. For **11** the chemical shift of NCH_2P was found between δ = 3.85 and δ = 4.10 ppm (in [D_4] methanol). The signals of the CH_2CN moiety were also found in the same range. The solvent effects seem to play a major role in the chemical shifts in the proton NMR. The proton-phosphorus coupling constants varied from $J_{P,H}$ = 10.5 Hz (NCH_2P; **9**) to 6.0 Hz (N^+CH_2P; **9**) and 6.5 Hz (N^+CH_2P; **10**). The phosphorus chemical shifts varied only little in range, δ = −81 ppm for all the compounds **8**–**11**, consistent with findings in the literature for similar compounds [7,16,21,22]. The carbon–phosphorus coupling constants to the two carbons adjacent to the tertiary nitrogen were also found to be similar for **8**, **9** and **10** ($J_{P,C}$ = 21.2 Hz). Also the coupling constants to the quarternary nitrogen were in the same range ($J_{P,C}$ = 34.5–35 Hz). In the ^{19}F NMR spectrum of compound **9**, one signal at δ = −80.29 ppm was observed [21]. The carbon–fluorine coupling was determined to be $J_{C,F}$ = 318.2 Hz. Molecular peaks for the PTA framework were found in the MALDI+ and in the ESI+ MS spectra for **8**, **9** and **11**. Compound **10** was only investigated by ESI+ spectrometry, showing a clear molecular peak. The presence of the triflate anion in compound **9** was proven by means of MALDI− MS.

For the analogous compound to **10** containing chloride as a counter ion, the chemical shifts in the phosphorus NMR were found to be at δ = −82.2 ppm [7], δ = −83.1 ppm [16b] and δ = −86.0 ppm [16a] all recorded with water as the solvent. The phosphorus NMR of **10** was recorded using [D_4] methanol, but the chemical shift of δ = −81.5 ppm is similar. The proton NMR chemical shifts of **10** (in [D_4] methanol) and [PTAbenzyl]Cl (in water) showed the same order of signals but with a slight high field shift of around $\Delta\delta$ = 0.15 ppm and only one down field shift of $\Delta\delta$ = 0.10 ppm for the signal of the benzylic protons [16b]. These minor differences may due to simple solvent effects. The phosphorus proton coupling constants of approximately $J_{P,H}$ = 6.4 Hz are nearly identical.

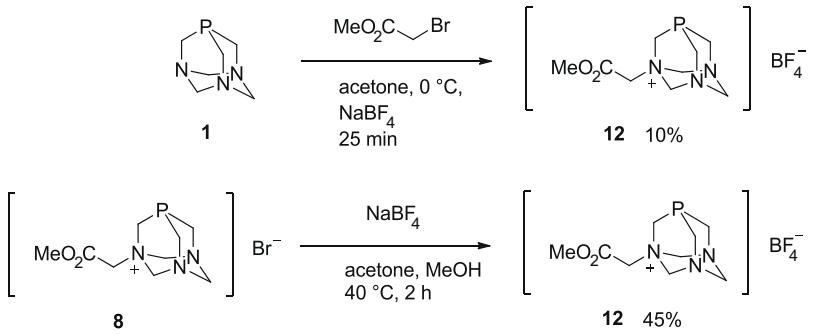
The water solubility was quantified by the slow addition of water *via* a 100 µl syringe to a stirred 100 mg sample of the respective compound at 25 °C. This process was repeated three times. Studies towards the solubility showed the same values for **9** and **10** (60 g/L) (Table 1, entries 2 and 3), which is lower than the solubility of PTA (236 g/L) [6]. The nitrile substituted compound **11** showed a two times higher water solubility value (123 g/L) compared to **9** and **10** (Table 1, entry 4). The highest value by far was observed for the ester containing compound **8**, with a value of nearly 1.5 kg/L! It showed a solubility 6 times higher than PTA itself and this is the highest value for a monoalkylated PTA salt reported so far. This finding is even more impressive with regards to the fact that the water solubility of NaBr and NH_4Br is 905 g/L and 740 g/L, respectively [32]. A high value for a PTA derived compound was reported for phenyl-(1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]dec-6-yl)methanol (PZA), with a solubility of $S_{20\ °C}$ = 1.05 kg/L [33]. The salt **8** is 1.5 times more soluble in water than the neutral compound PZA. For comparison of the solubility in water, [PTAbenzyl]Cl was prepared following a literature procedure [16b]. We found a high solubility of $S_{25\ °C}$ = 700 g/L. The solubility for this compound is around 11.7 times higher than that of **10**, which contains bromide as the counterion, and half as high as that found for compound **8**. The drawback of chloride containing compounds like [PTAbenzyl]Cl are the elevated temperatures and longer reaction times necessary for their preparation. Under the reaction conditions presented here, benzyl chloride did not react with PTA. Even after 24 h at room temperature no reaction was observed. Interestingly, the solubility depends more on the integrated counterion than on the substituent at the PTA framework. Introduction of bromide as a counterion resulted in an enhancement of the solubility by a factor of 24 compared to the triflate containing salt. A reason for this difference in solubility may be found in the huge difference of nucleophilicity of the counter ions [32,34]. Triflate, as a very weak nucleophile, is less likely to interact with a polar-protic solvent compared to bromide or chloride. Also separation into ion pairs is less likely for the triflate containing compound **9**.

For a proof of principles, we showed that the counterion could be exchanged. Already by the reaction of PTA with methyl bromoacetate in the presence of just 1 equivalent of $NaBF_4$ (under the same reaction conditions leading to **9**–**11**) compound **12** was obtained

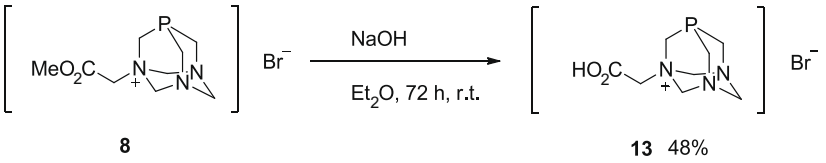
Table 1
Synthesis of the PTA salts **8**–**11**.

Entry	R	X	Temperature (°C)	*t* (min)	Compound	Yield[a] (%)	Solubility[b]
1	CO_2Me	Br	0	25	**8**	94	1450
2	CO_2Me	OTf	0	35	**9**	87	60
3	Ph	Br	0	25	**10**	89	60
4	CN	Br	−45	90	**11**	81	123

[a] Isolated yield.
[b] Solubility in water at 25 °C in g/L.



Scheme 2. Synthesis of **12** with BF_4^- as the anion.



Scheme 3. Synthesis of the carboxylic acid substituted derivative **13**.

in 10% yield with BF_4^- as the counter ion (Scheme 2). The purity was confirmed by elemental analysis. Alternatively compound **12** could be synthesized from **8** by an anion exchange reaction in a mixture of MeOH and acetone. The yield was thereby improved to 45%. One signal at $\delta = -154.07$ ppm was detected in the ^{19}F NMR spectrum. The remaining product was found to contain a mixture of both anions. The problem of the low yield can be approached by increasing the amount of added $NaBF_4$ and by fractional crystallization. As it was shown that the water solubility is heavily dependent on the counter ion (Table 1), it is important to state that by an exchange of the counter ion it is possible to tune the solubility properties of the corresponding compounds. Similar chemical shifts in the ^1H NMR spectrum of **12** were detected, as for **8**. The P–H coupling constant for the N^+CH_2P moiety was determined to be $J_{P,H} = 5.4$ Hz. The chemical shift of the phosphorus signal in the ^{31}P NMR spectrum was similar to **8** ($\delta = -82.37$ ppm).

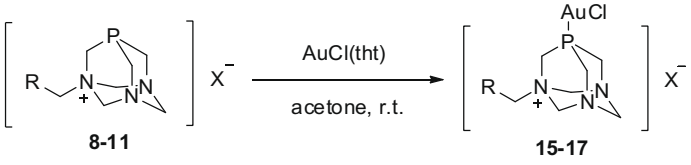
The transformation of the methylester moiety of compound **8** to the corresponding carboxylic acid was carried out under basic conditions in Et_2O at room temperature with sodium hydroxide as a base. The desired compound **13** was obtained in 48% yield (Scheme 3).

The hygroscopic compound **13** was identified by ^1H NMR, ^{31}P NMR spectroscopy, ESI+ mass spectrometry and HRMS spectrometry. The methylene moiety adjacent to the quarternary nitrogen and the acid group was detected at $\delta = 3.52$ ppm. In the ^{31}P NMR spectrum, one signal was detected at $\delta = -84.04$ ppm.

The solubility of **13** in water was determined to be higher than **8**. Because of its highly hygroscopic character, as yet not enough material has been synthesized to determine an exact value. Currently, investigations are underway to expand this general transformation to other PTA and DAPTA derivatives and to determine their water solubility, as well as investigations towards their potential application as bidentate ligands for transition metals.

3.2. Gold(I) complexes of N-alkylated PTA salts

The gold(I) complexes $[AuCl(PTACH_2R)]X$ (R = CO_2Me, phenyl; X = Br, OTf) are shown in Table 2. The preparation was carried out by replacement of tetrahydrothiophene (tht) from [AuCl(tht)] (**14**) by the PTA ammonia salt derivative in acetone at room temperature [35].



To perform the reaction, **14** was added to a solution of the PTA salt in acetone and stirred at room temperature under the exclusion of light for a suitable amount of time. Afterwards Et_2O was added to afford precipitation. Yields between 70% (Table 2, entry 3) and 85% (Table 2, entry 1) were obtained. Unfortunately compound **12** did not form the desired complex. Instead of a colorless solution, as in the other reactions, a brown suspension was obtained which indicated the formation of elemental gold. Variations of the reaction conditions did not lead to the formation of the desired gold complex, on the contrary, the decomposition of the starting material was always observed.

The gold complexes **15**–**17** showed comparable chemical shifts in their ^{31}P NMR spectra, at around $\delta = -31.5$ ppm, hardly depending on the solvent. The complexes **15** and **16** showed changes in chemical shifts in their ^1H NMR spectra compared to the corresponding sole phosphanes. The major difference was found for the signal of the methyl ester, which was shifted downfield to approximately $\delta = 3.9$ ppm compared to the sole phosphane **8**, and was similar to that found for **9**. Also the chemical shift of the methylene group next to the ester moiety was shifted, with $\Delta\delta = 0.3$ ppm in **15**. The complexes **9** and **16** showed almost the same chemical shift for this moiety ($\delta \approx 3.85$ ppm). As expected, proton signals of the methylene units next to the phosphorus atom were also affected. The shifts were found to be between $\Delta\delta = 0.45$ ppm (for NCH_2P) to $\Delta\delta = 0.5$ ppm (for N^+CH_2P) for complex **15** compared to **8**. Although measured in different solvents, similar effects were observed for **16** compared to **9**, and **17** compared to the parental phosphane **10**.

Table 2
Synthesis of the gold(I) complexes **15**–**17**.

Entry	R	X	*t* (h)	Compound	Yield[a](%)	Solubility[b]
1	CO_2Me	Br	48	**15**	85	48
2	CO_2Me	OTf	8	**16**	76	1.7
3	Ph	Br	14	**17**	70	4.7
4	CN	Br	14	**18**		

[a] Isolated yield.
[b] Solubility in water at 25 °C in g/L.

The IR spectra analysis of **15** showed intense bands at $\tilde{\nu} = 350$ and 320 cm^{-1}, and less intense bands at $\tilde{\nu} = 250$ and 230 cm^{-1}. The bands at about $\tilde{\nu} = 330$ cm^{-1} are characteristic for an Au–Cl-bond [36,37]. Vibrational bands at $\tilde{\nu} = 240$ cm^{-1} indicate a Au–Br bond [31,32]. Compound **16**, with a triflate counter ion, shows the same pattern of bands around $\tilde{\nu} = 240$ cm^{-1} as well, leading to the assumption that an Au–Cl bond is preferred in the present gold(I) complexes.

The formation of a gold-complex led to a drastic drop in solubility compared to the sole phosphanes. A comparison of the water solubility for complexes **15**–**17** showed the same graduation as was observed for the parental phosphane ligands. While the lowest solubility was found for **16** (1.7 g/L, Table 2, entry 2), the highest referred to complex **15** (48 g/L, Table 2, entry 1). Also the influence of the counter ion was found to be similar. The solubility of **8** was 24 times higher than that of **9**. Compound **15** is 28 times more soluble in water than **16**. The water solubility for compound **17** was determined to be 4.7 g/L, which is slightly higher than that of **16**. However, **15** is more than 10 times more soluble in water. Compared to the parental phosphanes, the effect of the counter ion in the gold(I) complexes overcompensates the substitution effect at the PTA framework, as reflected in the data of Table 2.

Some gold(I) PTA complexes were found to show possible luminescent properties [27]. Compounds **15**–**17** were investigated for their luminescent properties in the solid state and as an aqueous solution. Measurements were taken at −20, 0 °C (solid state) and at room temperature (solid state and solution). The tested compounds showed no luminescence. It has already been stated that similar compounds like [Au(PTA)]X (X = Cl, Br, I, Me, Ph) and [Au(H-PTA)]X_2 (X = Cl, Br) are not luminescent as aqueous solutions, although [Au$(PTA)_3$]Cl was found to be strongly luminescent [38].

Table 3
Selected bond lengths (Å) and angles (°) for 1-methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.$1^{3,7}$]decane triflate [$PTACH_2CO_2Me$]OTf (**9**).

P(1)–C(3)	1.577(7)	C(3)–P(1)–C(4)	106.6(4)
P(1)–C(4)	1.640(5)	C(3)–P(1)–C(2)	98.0(2)
P(1)–C(2)	1.814(4)	C(4)–P(1)–C(2)	96.3(2)
N(2)–C(2)	1.425(11)	C(2)–N(2)–C(4)	112.9(9)
N(2)–C(4)	1.663(17)	C(2)–N(2)–C(3)	109.9(8)
N(2)–C(3)	1.702(14)	C(4)–N(2)–C(3)	100.1(8)
N(1)–C(5)	1.490(4)	C(5)–N(1)–C(2)	112.47(14)
N(1)–C(2)	1.527(3)	C(5)–N(1)–C(1)	105.2(2)
N(1)–C(1)	1.547(4)	C(2)–N(1)–C(1)	108.10(15)
O(1)–C(6)	1.197(4)	O(1)–C(6)–O(2)	125.2(3)
O(2)–C(6)	1.325(4)	O(4)–S(1)–O(3)	114.90(11)
O(2)–C(7)	1.445(4)	O(4)–S(1)–C(8)	103.45(19)
S(1)–O(3)	1.434(2)	F(2)–C(8)–F(1)	108.3(2)
S(1)–C(8)	1.813(4)	F(2)–C(8)–S(1)	112.0(2)
C(8)–F(2)	1.313(3)		

3.3. X-ray structure determination of 1-methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.$1^{3,7}$]decane triflate [$PTACH_2CO_2Me$]OTf (**9**)

Single crystals suitable for X-ray diffraction analysis of compound **9** were obtained from water by slow evaporation. The crystal taken for X-ray analysis was a colorless block having dimensions 1.5 × 1.0 × 0.5 mm. Data collection was performed on a Nicolet P3 with Mo Kα radiation at 293 K and a wavelength of 0.71073 Å. The structural refinement was done on F^2 (SHELXL97) [39]. The refinement method referred to full-matrix least-squares on F^2. 3603 reflections were collected with 2506 [$R_{int} = 0.0469$] unique ones. The largest diffraction peak and hole were at 0.321 and −0.271 $Å^{-3}$. Goodness of fit was determined on F^2 1.050 and $F(0\,0\,0)$ 784. The θ range for data collection was 2.05–30.00°. Completeness to $\theta = 30.00°$ was 100.0%. Limiting indices were at $0 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 11$ and $-21 \leqslant l \leqslant 16$. R indices of all data were found to be $R_1 = 0.0794$ and $wR_2 = 0.1679$. The final R indices [$I > 2\sigma(I)$] were $R_1 = 0.0578$ and $wR_2 = 0.1561$. Compound **9**, with the empirical formula $C_{10}H_{17}F_3N_3O_5PS$ and molecular weight of $M = 379.30$ g/mol and a calculated density of 1.565 mg/m^3, crystallized as orthorhombic in the asymmetric unit of the centrosymmetric space group *Pnma*. The unit cell dimensions are $a = 12.953(2)$ Å and $\alpha = 90°$, $b = 7.9915(15)$ Å and $\beta = 90°$ and $c = 15.550(2)$ Å and $\gamma = 90°$ with a cell volume of 1609.6(5) $Å^3$. Not all molecules showed the same orientation to the anion. Each of the halves of the molecules in the elementary cell, which

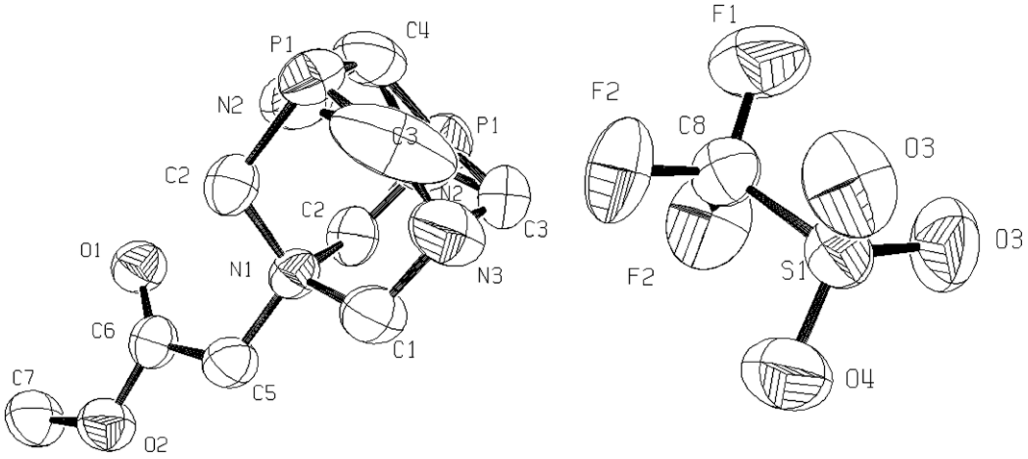


Fig. 1. Thermal ellipsoid representation of 1-methoxycarbonylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.$1^{3,7}$]decane triflate [$PTACH_2CO_2Me$]OTf (**9**). Thermal ellipsoids are drawn at the 50% probability level.

consists of four cation–anion pairs, showed different orientations towards each other. The symmetry operator x, $0.5 - y$, z completes the cation and the anion. This symmetry condition forces also a disorder of the nitrogen N2 and the phosphorus P1. These positions were changed in the cation, *vice versa,* characterized by population factors of 0.5 each. The orientation of the fluorine- and oxygen atoms of the trifluoromethane sulfonate anion shows, as expected, a staggered conformation.

The thermal ellipsoid representation of the solid state of compound **9** is shown in Fig. 1. The corresponding selected interatomic distances and angles are given in Table 3. It is problematical to carry out a quantitative discussion of bond geometries around the disordered atoms N2 and P1. Some N–C distances are lengthened (N2–C3, N2–C4) and some P–C distances are shortened (P1–C3, P1–C4). For example the P1–C3 distance is observed to be 1.577(7) Å, which is about 0.25 Å too short with respect to nominal aliphatic P–C distances. On the other hand, the N2–C3 distance is 1.70(1) Å which is about 0.25 Å too long compared to nominal 3 covalent N–C distances. This is a result of the disorder, which 'smears' the electron density between P1 and N2. (The distance between P1 and N2 is only 0.4 Å, which is much shorter than the resolution of the data (0.7 Å)).

4. Conclusion

We have presented new routes and transformations at the PTA framework to gain access to new *N*-alkylated PTA derivates and have shown that these compounds can be used as ligands in gold(I) complexes. An X-ray structure analysis of a new PTA salt has been presented. The exchange of the counter ion, as well as transformations at the introduced moiety were successfully performed. Also, a new class of highly water soluble, possibly bidentate PTA based ligands were discovered. Based on these results, the library of water-soluble phosphane ligands could be expanded and would allow a straight forward preparation of a series of different metal complexes, permitting the tuning of the electronic properties of the central metal ion. Studies on the solubility in water discovered the highest value so far found for a mono-*N*-alkylated PTA salt. The next step would be the preparation of PZA salts which should then lead to compounds that should show even higher solubilities. The preparation of other PTA salt based gold-complexes and studies towards their water solubility and their luminescent properties are currently under way.

5. Supplementary data

CCDC 762475 contains the supplementary crystallographic data for **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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