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Borane adducts of the water soluble phosphine PTA (PTA = 1,3,5-triaza-7-phosphaadamantane)

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Abstract

Boronation of the water soluble phosphine PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) in dry THF easily affords the *N*-boronated adduct *N*-*B*-PTABH₃ which represents the first *N*-coordinated adduct of this popular water soluble phosphine (*N*-*B*-PTABH₃ = 1-boranyl-1,3,5-triaza-7-phosphaadamantane). In situ ³¹P NMR spectroscopy suggests the occurrence of a stepwise boronation resulting in the addition of as many as four equivalents of BH₃ to PTA to give the polyboranyl species N_x , P_y -*B*-PTA(BH₃)_(x+y) (x = 1-3, y = 0, 1). Hydrolysis of the monoboranyl adduct occurs slowly in the presence of water yielding back PTA and boric acid, H₃BO₃. © 2006 Elsevier B.V. All rights reserved.

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Among water soluble phosphines, particular attention has been recently paid to the cage-like tertiary phosphine l,3,5-triaza-7-phosphaadamantane (PTA, I) [1] whose high solubility in water has been ascribed to the extensive participation of its three nitrogen atoms in hydrogen bonding interactions with water molecules [2]. The attractiveness of this ligand stems from its unique properties which make it an hydrosoluble ligand amenable for aqueous biphasic catalysis and metal carrier in biological systems. Indeed, with respect to most of the commonly used water soluble phosphines [3], PTA is a neutral and air-stable molecule which is both sterically (the cone angle is 103°) and electronically comparable with the extremely air and moisture sensitive PMe₃ [1].

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Following the recent interest in PTA chemistry, a variety of PTA metal complexes, invariably coordinated via the bridgehead P-atom, have been synthesized [1,4–6] and successfully used in aqueous phase catalysis [1,4e,4f,5] as well as in biologic tests aimed at evaluating their activity as selective anticancer agents [1,4a,4h,6]. In contrast, little efforts have so far been addressed to explore the coordination properties of the potentially multidonor triaza-phosphaadamantane moiety. Electrophiles such as H⁺ and R⁺ [R = Me, Et, CH₂Ph, CH₂CH₂CH₂CH₂I [1], CH₂C₆H₄(*p*-MeO)[7]] are known to selectively bind to one nitrogen atom, but rather surprisingly N-coordination of PTA was never observed until our recent report describing the

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straightforward formation of the heterobimetallic coordination polymer [{CpRu(PTA)₂(dmso- κS)} {AgCl₂}] by the reaction of silver triflate with [CpRu(PTA)₂Cl] in DMSO [8]. In such water soluble polymer, the AgCl₂ anion links two nitrogen PTA atoms of two distinct {CpRu(PTA)₂} units, whereas the PTA P-atoms are coordinated to the ruthenium centre.

Herein, we report on the simple preparation of new Nadducts of PTA which pave the way to the synthesis of new PTA derivatives which, in turn, might be successfully used as modified versions of PTA in organometallic chemistry and catalysis as well as in medicinal chemistry [9].

The plain reaction of 1.1 excess of BH₃·THF (1 M in THF) with PTA in THF gives, after work-up, a white solid of formula $[P(CH_2NCH_2)_2\{CH_2N(BH_3)CH_2\}]$ (*N-B*-PABH₃; (1)) (N-B-PTABH₃ = 1-boranyl-1,3,5-triaza-7phosphaadamantane) which was characterized by conventional spectroscopic techniques and elemental analysis (Scheme 1) [10]. The coordination of borane to nitrogen rather than phosphorus is indirectly confirmed by the sharp ³¹P NMR resonance [$\delta = -94.85$, $\Delta \delta = \delta_{PTA} \delta_{N-B-\text{PTABH}_3} = -101.28$ to -94.85 = 6.43], and directly inferred from inspection of both the IR and of the ${}^{13}C{}^{1}H$ NMR spectra [11]. A diagnostic B-N stretching vibration is visible in the solid state IR spectrum (KBr) at 1171 cm⁻¹ [12], while the carbon-13 NMR spectrum shows the loss of the ternary symmetry of PTA showing four different CH₂ resonances in keeping with the regioselective delivery of borane to one nitrogen atom. The ¹¹B NMR spectrum displays a



quartet at -10.55 ppm (${}^{1}J_{BH} = 98.3$ Hz), which matches the literature values reported for other aminoboranes [13].

Monitoring the reaction between PTA and BH₃. THF by ³¹P{¹H} NMR provides useful mechanistic information and shows that all of the four donor atoms of PTA may coordinate borane, fully exploiting the coordination capabilities of PTA (Scheme 1). Thus, adding more than one equivalent of borane to a THF solution of PTA shows that the formation of 1 is followed by that of the bis-boranyl species 2 existing as a pair of coordination isomers depending on whether the boronation occurs either at a second nitrogen atom (2N, δ -92.37) or at the phosphorus (2P, δ -43.41). Further addition of borane produces a similar pair of tris-boronated PTA isomers (3N, δ –93.45; 3P; δ -34.01). Eventually, when a large excess of BH₃ is added to the solution, the signal due to the tetrakis-boranyl adduct 4 (δ -28.83) becomes the only resonance visible in the NMR spectrum. Remarkably, the signals of the P-boranyl complexes 2P, 3P and 4 are highly deshielded with respect to the N-boranyl adducts $[\Delta \delta = \delta_{PTA} \delta_{(P-B-\text{PTABH}_3)\text{ave}} = -101.28 \text{ to } -35.42 = 65.86 \text{ and feature}$ the typical broadness of boronated phosphines [11]. Only the first equivalent of borane is transferred to the phosphaadamantane cage with complete regioselectivity preferring one of the nitrogen atoms rather than the bridgehead phosphorus [14]. In contrast, the bis- and tris-boranyl adducts 2 and 3 are formed without regioselective control. Thus, for 2 *N*-coordination is favoured whereas for the tris-boranyl species **3**. *P*-coordination represents the preferred pathway. Fig. 1 shows the progress of the PTA boronation as a function of the equivalents of BH3 THF added to a THF solution of PTA (36 mg, 0.23 mmol, in 0.8 ml of THF locked with a CDCl₃ capillary) with the different species quantified by careful NMR integration of their ³¹P NMR resonances.

Attempts to isolate 2, 3 or 4 in the solid state failed because when THF solutions enriched in these polyboranated species were evaporated to dryness, only the monoboranyl adduct 1 could be obtained as a solid.

Complex 1, dissolved in acetone, slowly reacts with water to give back the free PTA and orthoboric acid (Scheme 1). The reaction is accelerated at higher temperature and completes in ca. 48 h when a sample of 1 in acetone/H₂O (1:1 v/v) is kept at 80 °C. The presence of H₃BO₃ in the hydrolised solution was confirmed by the appearance in the IR spectrum of absorptions ascribable to B–O bonds $(1241 \le v_{BO} \le 1435 \text{ cm}^{-1})$ replacing those assigned in 1 to B–H stretchings (2386 $< v_{BH} < 2275 \text{ cm}^{-1}$). In the ¹¹B NMR spectrum, a signal at 19.52 ppm was attributed to boric acid [13]. The transformation of 1 into PTA and H₃BO₃ is quantitative under the experimental conditions used and resembles the well-known acid-catalysed hydrolysis of aminoboranes for which a mechanism involving the reversible protonation of 1 with release of H_2 and formation of B(OH)₃ has been proposed [15].

The general reactivity and, in particular, the coordination properties of 1 and the higher boronated adducts (2,4) are under investigation in our laboratories [9]. Preli-



Fig. 1. Distribution of the different PTA borane adducts (1-4) as a function of the equivalents of BH₃.THF added to a THF solution of PTA.

minary studies indicate that the boronated PTA-adducts behave as monofunctional *P*-ligands towards a variety of transition metal ligands including rhodium, iridium and ruthenium. In some cases the new metal complexes exhibit a substantial enhancement of their water solubility in comparison to the related PTA species, which could make them suitable as potential water soluble catalysts and in medicinal chemistry. Catalytic studies aimed at exploring the performance of these ligands in both water and under biphasic aqueous conditions are in progress.

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found C 42.17, H 8.80, N 24.15%. IR (KBr pellets, cm⁻¹): $v_{BH} = 2275$ (m), 2317 (m), 2386 (s); $v_{BN} = 1171$ (s). ¹H NMR (acetone- d_6 , 294 K, 400.13 MH_z, TMS ref): δ (ppm) 0.77–1.99 (br, 3H, BH₃); 3.70–4.20 (m, 8H, CH₂); 4.30–4.53 (m, 4H, CH₂). ¹³C{¹H} NMR (acetone- d_6 , 294 K, 100.68 MHz, TMS ref): δ (ppm) 43.42 (d, C_β, ¹ $J_{CP} = 19.3$ Hz); 51.07 (d, C_z, ¹ $J_{CP} = 25.8$ Hz); 75.10 (d, C_y, ³ $J_{CP} = 1.1$ Hz); 77.69 (d, C_δ, ^{3} $J_{CP} = 0.4$ Hz). ¹¹B NMR (acetone- d_6 , 294 K, 128.3 MHz, BF₃.OEt₂ ref): δ (ppm) –10.55 (q, ¹ $J_{BH} = 98.3$ Hz, BH₃). ³¹P{¹H} NMR (acetone- d_6 , 294 K, 162.02 MHz, 85% H₃PO₄ ref): –94.85 ppm (s).}

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