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Two new water-soluble derivatives of 1,3,5-triaza-7-phosphaadamantane (PTA): Synthesis, characterization, X-ray analysis and solubility studies of 3,7-diformyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane and 1-pyridylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane bromide

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Abstract

Two water-soluble phosphines, 3,7-diformyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (**1**, DFPTA) and 1-pyridylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane bromide (**2**, [pymePTA]Br), have been respectively, prepared by reacting 1,3,5-triaza-7-phosphaadamantane (PTA) with formic anhydride and bromomethylpyridine. Compound **1** is only the second acyl derivative of PTA to be prepared while **2** is only the second derivative of PTA reported that contains an aromatic appendage. Both compounds were characterized by elemental analysis, FAB-MS, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and single crystal X-ray diffraction. This analysis showed that the formamide groups of **1** were in an *anti* confirmation in solution but in a *syn* confirmation in the solid state. The solubilities of **1** and **2** were examined in common organic solvents and water. It was found that 1.1 M aqueous solutions of **1** could be prepared while 2.4 M solutions of **2** were produced. The greater solubility of **2** was likely due to its ionic nature.

Keywords: Phosphine; Ligand; Water; Water-soluble; 1,3,5-Triaza-7-phosphaadamantane

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1. Introduction

Employing water as a medium for organic transformations is advantageous for several reasons. First, the process alleviates the use of flammable, volatile, and carcinogenic solvents that are potentially hazardous to the environment and the employees of the chemical fields [1]. Second, water is the most abundant liquid on earth, and as such, it is inexpensive [2]. Third, as Breslow [3] and many others [4] have clearly shown, the rates, yields, and selectivities of some organic transformations, such as the Diels–Alder reaction, are enhanced in water. Fourth, in metal-mediated transformations, simple phase extraction allows the metal free, organic products to be easily separated from the intact catalyst [5]. Consequently, the expensive metal catalyst may be recovered and recycled. This is generally not possible with metal-catalyzed reactions in organic solvents because the separations often involve thermal processes, which may lead to deactivation or decomposition of the complex [6].

Transition metals are often made water-soluble by ligation with phosphines that contain ionic or polar functionalities such as sulfonates, carboxylates, and hydroxyls [7]. One ligand that contains amine functionality is 1,3,5-triaza-7-phosphaadamantane (PTA) [8], and this phosphine

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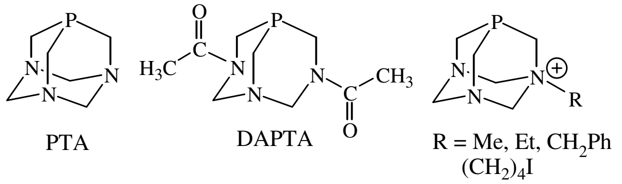

Fig. 1. 1,3,5-Triaza-7-phosphaadamantane (PTA) and some of its derivatives.

has recently been extensively studied [9]. While the water-solubility of PTA is approximately 1.5 M [10], the solubility of its complexes is variable and is sometimes extremely low [11]. This is problematic in that its ultimate utility is as a ligand for aqueous catalysis. In fact, PTA complexes have recently been shown to catalyze many hydrogenations reactions [12] and the intramolecular hydroamination of alkynylamines [11a,13] in water (see Fig. 1).

In an effort to enhance the water-solubility of the phosphine and its metal complexes, PTA has been derivatized by reacting it with acetic anhydride [10], MeI [8] or $MeOSO_2CF_3$ [14], EtI [15], $I(CH_2)_4I$ [16], and $PhCH_2Cl$ [17] to respectively form the di-*N*-acylated compound 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA), and the *N*-alkylated compounds [PTA(R)]X (R = Me, Et, $(CH_2)_4I$, and CH_2Ph). A library of water-soluble ligands, such as this, is important in that it allows for the preparation of a series of metal complexes that differs by only the phosphine, and this may permit the electronic properties of the compounds to be tuned. For example, it was recently shown that the oxidation potentials of $[CpRuL_2X]$ (L = PTA, $PTA(Me)^+$; X = I, Cl) complexes could be raised by over 300 mV by switching from PTA to $[PTA(Me)]^+$ [18].

To further add to the existing library of water-soluble phosphines, the di-*N*-formylated analog of DAPTA, 3,7-diformyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (**1**, DFPTA), and the *N*-methylpyridyl derivative of PTA, 1-pyridylmethyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane bromide (**2**, [pymePTA]Br) were prepared, fully characterized, and their solubilities explored. Compound **1** is only the second acyl derivative of PTA to be prepared while **2** is only the second derivative of PTA reported that contains an aromatic appendage. The findings of this study are presented herein.

2. Experimental

2.1. Methods, measurements, and materials

All manipulations were carried out under a purified N_2 atmosphere with use of standard Schlenk techniques unless otherwise noted. This airless procedure was used even though the final compounds were air stable. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Fast atom bombardment mass spectrometric (FAB-MS) experiments were carried out at Michigan State University with the use of a JEOL HX-110 double-focusing mass spectrometer. Infrared spectra were measured in KBr pellets on a Jasco 460 Plus spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 MHz and 75.5 MHz respectively, with use of a Bruker ARX 300 MHz spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz on a Varian Mercury 300 MHz spectrometer. The ^{13}C and ^{31}P spectra were run with proton decoupling and ^{31}P spectra are reported in ppm relative to an external H_3PO_4 standard, with positive shifts down field. ^{13}C NMR spectra are reported in ppm relative to external tetramethylsilane (TMS), with positive shifts downfield. The solvents were distilled and dried prior to use. Formic acid, 1,3-dicyclohexylcarbodiimide (DCC), and 2-bromomethylpyridine hydrobromide were obtained from Aldrich and used without further purification. 1,3,5-Triaza-7-phosphaadamantane (PTA) was prepared as described in the literature [8].

2.2. Synthesis of compounds

2.2.1. 3,7-Diformyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]heptane (*1*, DFPTA)

A 100 mL Schlenk flask was charged with a 6.56 g (31.8 mmol) sample of 1,3-dicyclohexylcarbodiimide (DCC) and 25 mL diethyl ether and put into a −5 °C KCl-ice bath. A separate 100 mL Schlenk flask was charged with 2.50 mL formic acid (66.3 mmol) and 25 mL diethyl ether and put into a −5 °C KCl-ice bath. The DCC solution was added to the formic acid under N_2 over a 10 min period to form a colorless solution of formic anhydride and solid 1,3-dicyclohexylurea. A 250 mL round-bottom flask equipped with a jacketed frit, gas inlet, and rubber septum was charged with 1.01 g PTA (6.43 mmol) and 20 mL H_2O. The jacketed frit and round-bottom flask were then cooled to −5 °C. After stirring for 90 min at −5 °C, the formic anhydride/1,3-dicyclohexylurea slurry was transferred under N_2 to the jacketed frit. This mixture was filtered over a 10-min period into the 250 mL round-bottom flask to remove the 1,3-dicyclohexylurea. After stirring for 15 min at −5 °C, vacuum was applied to the reaction for 30 min to remove the diethyl ether. After this time, the solution was stirred at 0 °C for an additional 30 min. The cloudy solution was cold filtered in the air into a 100 mL round bottom flask that was previously cooled to 0 °C. Over a 10 min period, 6.85 mL of cold $NHEt_2$ (66.2 mmol) was added dropwise to deprotonate any remaining formic acid. The solution was transferred to the rotary evaporator and vacuum was applied at 5 °C. Under vacuum, the solution was allowed to gradually warm to 20 °C and ultimately to 35 °C. The solvents were removed in vacuo to form a white residue. 10 mL of 95% EtOH was added to the flask to dissolve any ammonium salts that may have formed during the workup. The slurry was stirred for 15 min and filtered on a medium frit. The resulting white solid was washed with EtOH (2 × 5 mL), DMSO to remove unreacted PTA