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1,3,5-Triaza-7-phosphaadamantane (PTA) ligated iridium(I) complexes as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine in water

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Abstract

The water-soluble complex [Ir(COD)(PTA)$_3$]Cl (**1**, PTA = 1,3,5-triaza-7-phosphaadamantane) was prepared by the reaction of [IrCl(COD)]$_2$ with six equivalents of PTA under a nitrogen atmosphere. Compound **1** was fully characterized in solution and the solid state. **1** crystallized in the monoclinic space group C2/c with $a = 29.648(9)$ Å, $b = 11.238(2)$ Å, $c = 19.930(2)$ Å, and $\beta = 96.55(2)°$. Complex **1** and the related Ir(I) compounds, [IrCl(CO)(PTA)$_3$] (**2**) and [Ir(CO)(PTA)$_4$]Cl (**3**), were active catalysts in the intramolecular hydroamination of 4-pentyn-1-amine in water. This is the first reported study of the Ir(I) mediated transformation in aqueous media.

Keywords: Water; Phosphine; Iridium; 1,3,5-Triaza-7-phosphaadamantane; Intramolecular hydroamination

The increasing cost of waste disposal and the need to preserve the environment have caused the chemical, pharmaceutical, and petroleum industries to re-evaluate their present production and distribution methods, and where possible, switch to more "green" processes [1]. Green methodologies are often considered to be those that reduce or eliminate the use or production of environmentally hazardous substances [2]. This may include the use of renewable resources, alternative modes of packaging and distribution, and modifications in manufacturing and processing [3]. One such modification is the use of environmentally benign solvents, such as supercritical CO$_2$ [4] and water [5].

We have recently reported that PTA-ligated (PTA = 1,3,5-triaza-7-phosphaadamantane) Pt(II) [6] and Pd(II) [7] complexes function as catalysts for the intramolecular hydroamination of terminal alkynylamines in water. The hydroamination reaction is environmentally and economically important in that it is a 100% atom efficient process [8] for catalytically preparing higher substituted amines that are important intermediates for the production of polymers, natural products, solvents, and surfactants [9]. In the case of the intramolecular hydroamination, the end products are pharmaceutically important N-heterocycles [10], and hence this process has recently received quite a bit of attention [11].

The work of Field and Messerle [12] has recently shown that Ir(I) complexes may function as intramolecular hydroamination catalysts. Therefore, in an effort to expand our present study of aqueous phase catalysis, we have recently investigated the abilities of PTA ligated Ir(I) compounds to mediate the cyclization of terminal alkynylamines in water. We wish to report on this study that involved the synthesis and characterization of [Ir(COD)(PTA)$_3$]Cl (**1**), as well as the use of **1**, and the related compounds, [IrCl(CO)(PTA)$_3$] (**2**) and [Ir(CO)(PTA)$_4$]Cl (**3**), as aqueous phase catalysts in

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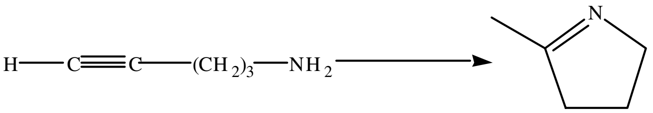
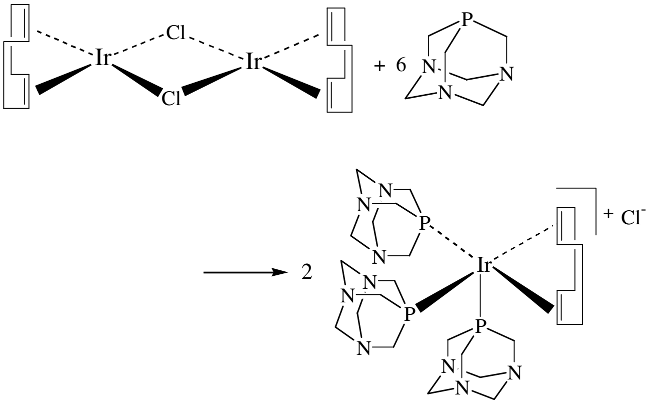
the intramolecular hydroamination of 4-pentyn-1-amine at 50 °C (Reaction (1))



(1)

The 1,3,5-triaza-7-phosphaadamantane (PTA) ligated complex [Ir(COD)(PTA)$_3$]Cl (**1**) [13], was produced in high yield by reacting [IrCl(COD)]$_2$ (COD = 1,5-cyclooctadiene) [14] with six equivalents of PTA [15] in CH_2Cl_2. Almost immediately, the complex precipitated from the solution as an air-stable solid.



(2)

Fast atom bombardment – mass spectrometry and elemental analysis were employed to confirm the empirical formula of **1**. The ^{31}P NMR spectrum of **1** in D_2O exhibited only one sharp singlet ($\delta = -86.8$ ppm) thus indicating that the phosphines are fluxional on the NMR timescale. This behavior is common with [Ir(COD)P$_3$]$^+$ complexes [16] and is likely due to a Berry pseudo-rotation [17].

Compound **1** was crystallographically characterized in order to better understand its geometry. Table 1 contains the collection parameters and crystallographic data of the experiment [18].

Crystals of [Ir(COD)(PTA)$_3$]Cl that were suitable for X-ray analysis were grown by the slow diffusion of ethanol into an aqueous solution of **1**. It was found that **1** crystallized with three water molecules in the C2/c space group. The cationic structure is shown in Fig. 1. Selected interatomic distances and angles of **1** are presented in Table 2, and additional crystallographic data are provided as supplementary material.

Table 1
Crystallographic data for [Ir(COD)(PTA)$_3$]Cl · 3H_2O (**1** · 3H_2O)

Empirical formula	$IrClO_3P_3N_9C_{26}H_{54}$
Formula weight (amu)	861.34
Crystal color, habit	colorless, plate
Crystal dimensions (mm)	0.50 × 0.48 × 0.20
Crystal system	monoclinic
Space group	*C*2/*c*
Cell parameters at *T* (K)	293
a (Å)	29.648(9)
b (Å)	11.238(2)
c (Å)	19.930(3)
β (°)	96.55(2)
V (Å^3)	6597(3)
Z	8
Calculated density (Mg m^{-3})	1.734
F(000)	3488
Absorption coefficient (mm^{-1})	4.319
Absorption correction	psi-scan
θ range for collection (°)	2.06 to 25.96
Number of reflections collected	6573
Number of independent reflections	6446
Refinement method	full matrix least squares on F^2
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0430$, $wR_2 = 0.1080$
R indices (all data)	$R_1 = 0.0705$, $wR_2 = 0.1206$
Goodness of fit on F^2	1.008
Largest difference peak and hole (e Å^{-3})	1.613 and −1.150

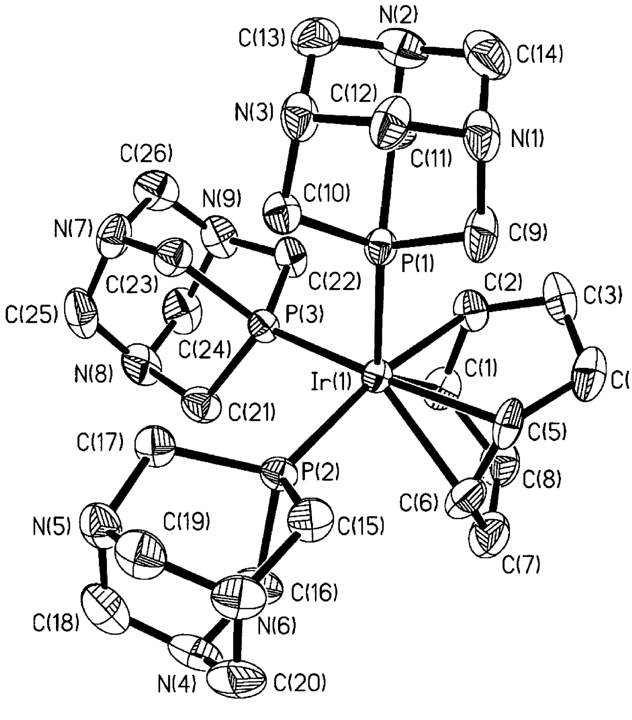


Fig. 1. Thermal ellipsoid representation of [Ir(COD)(PTA)$_3$]Cl · 3H_2O (**1** · 3H_2O) with solvent molecules and anions omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The structure of **1** may best be described as a distorted square-pyramid with P(1) occupying the axial site and P(2), P(3), and the COD ligand residing in the basal sites. This may be more clearly seen if each C═C of the COD ligand is defined as a centroid. When this is done, the midpoint between C(1) and C(2) becomes X(1A), and the midpoint between C(5) and C(6) becomes X(1B). As Fig. 2 illustrates, P(2), P(3), X(1A) and X(1B) are almost coplanar with an average deviation of 0.07 Å from the plane, and the Ir is displaced 0.47 Å above this plane. The bond angles between the apical and basal phosphorous atoms are 99.65(7)° and 95.93(7)° for P(1)–Ir–P(2) and P(1)–Ir–P(3), respectively. The angles between P(1) and