Coordination Chemistry Reviews 355 (2018) 328–361

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Coordination chemistry of 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane (PTA) and derivatives. Part III. Variations on a theme: Novel architectures, materials and applications

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ARTICLE INFO

Article history:
Received 12 June 2017
Received in revised form 18 September 2017
Accepted 22 September 2017
Available online 31 October 2017

Dedicated to Prof. Pierre Braunstein, in recognition of his outstanding contributions in organometallic chemistry, homogeneous catalysis and much more, on occasion of his 70th birthday.

Keywords:
1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane
Water soluble ligands
Coordination chemistry
X-ray crystallography
Catalysis
Materials science
Medicinal inorganic chemistry

ABSTRACT

This review paper covers the recent (2010–2017) synthetic modifications of the water soluble cage-like aminophosphine ligand 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane (PTA) and their application in coordination chemistry, with a focus on applications in the fields of selected catalytic processes, 1D–3D materials and mention to novel use as anticancer and antimicrobial agents in medicinal inorganic chemistry.

Abbreviations: PTA, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane; HPTA, 1-H-1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane; mPTA, 1-methyl-1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane; PTA—Bn, 1-benzyl-1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane; PTA═S, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane-7-sulfide; PTA═O, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane-7-oxide; PTA—SO_2, 2-thia-1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane-2,2-dioxide; dmoPTA, 3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; HdmoPTA, 3,7-H-3,7-dimethyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; DAPTA, 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; PZA, phenyl-(1,3,5,-triaza-7-phosphatricyclo[3.3.1.1]dec-6-yl)methanol; PZA-NMe_2, 4′-(dimethylamino)phenyl-(1,3,5,-triaza-7-phosphatricyclo[3.3.1.1]dec-6-yl)methanol; CAP, 1,4,7-triaza-9-phosphatricyclo[5.3.2.1^{4,9}]tridecane; p-cymene, η^6-$C_{10}H_{14}$; Tp, κ^3-tris(pyrazolyl)borate; Tpm, κ^3-tris(pyrazol-1-yl)methane; Tpms, tris(pyrazol-1-yl)methanesulfonate; *m*TPPMS, *meta*-(triphenylphosphine)monosulfonate; *m*TPPTS, *meta*-(triphenylphosphine)trisulfonate; THP, tris(hydroxymethyl)phosphine; RAPTA, generic Ru–arene-PTA complex; RAPTA-C, [$RuCl_2$(p-cymene)(PTA)]; Na[$H_2B(pz)_2$], κ^2N-dihydrobis(pyrazolyl)borate sodium salt; K[$H_2B(tz)_2$], dihydrobis(triazolyl)borate potassium salt; K[$H_2B(tzNO_2)_2$], dihydrobis(3-nitro-1,2,4-triazolyl)borate potassium salt; $CH_2(pz)_2$, bis(pyrazol-1-yl)methane; H[bdmpza], κ*N*,*N*,*O*-bis(3,5-dimethylpyrazol-1-yl)acetic acid; Hba, benzoic acid; Hcba, 4-cyanobenzoic acid; Haba, 2-aminobenzoic acid; H_2tpa, terephthalic acid; H_2suc, succinic acid; H_2adip, adipic acid; H_2mal, malonic acid; Hchc, cyclohexanecarboxylic acid; H_2chdc, 1,4-cyclohexanedicarboxylic acid; H_4chtc, 1,2,4,5-cyclohexanetetracarboxylic acid; H_2pga, 3-phenylglutaric acid; H_2dmga, 3,3-dimethylglutaric acid; H_2pma, phenylmalonic acid; bipy, 2,2′-bipyridine; dtbpy, 4,4′-di-*tert*-butyl-2,2′-bipyridine; phen, 1,10-phenanthroline; neocup, 2,9-dimethyl-1,10-phenanthroline; dione, 1,10-phenanthroline-5,6-dione; tht, tetrahydrothiophene; Spy, pyridine-2-thiolate; Spyrim, pyrimidine-2-thiolate; Smepyrim, 4-methylpyrimidine-2-thiolate; SMe_2pyrim, 4,6-dimethylpyrimidine-2-thiolate; MNP, metal nanoparticles; salphen, *N*,*N*′-bis(salilcylidene)imine-1,2-phenylenediamine; MOF, metal organic framework; LC_{50}, median lethal concentration required to kill half the members of a tested cell population after a specified test duration; LD_{50}, median lethal dose required to kill half the members of a tested cell population after a specified test duration; GI_{50}, concentration for 50% of maximal inhibition of cell proliferation; IC_{50}, half maximal inhibitory concentration for a specific biological or biochemical function; NMR, multiplicities; s, singlet; d, doublet; dq, doublet of quartets; t, triplet; dt, doublet of triplets; tt, triplet of triplets; br, broad; brs, broad singlet; q, quartet; sept, septuplet; m, multiplet; TON, turnover number; TOF, turnover frequency (h^{-1}); ^{t}BuDAD, *tert*-butyldiazadiene; OTf^-, $CF_3SO_3^-$, triflate anion; CORM, carbon monoxide releasing molecules; Mb, myoglobin; phen, 1,10-phenanthroline; pbt, 2-(pyridyl)benzothiazole; CV, cyclic voltammetry; TCNE, tetracyanoethylene; DMAD, dimethylacetylenedicarboxylate; DEAD, diethylacetylenedicarboxylate; DBMH, dibenzoylmethane; HRMS, high resolution mass spectrometry; EPR, electron spin resonance spectroscopy; ET-dmbaH, 17-α-[4′-ethynyldimethylbenzylamine]-17-β-testosterone.

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https://doi.org/10.1016/j.ccr.2017.09.024
0010-8545/

Contents

1. Introduction

After the first comprehensive reports on the chemistry of 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane (PTA, also denoted in the literature as 1,3,5-triaza-7-phosphadamantane) published in 2004 and 2010, respectively [1], the use of this cage-like water-soluble phosphine and its derivatives, often obtained by cage functionalisation and introduction of different substituents (Chart 1) was expanded further by many research groups worldwide, beyond their established role as ligands for coordination chemistry to noble and base metals. Further to use in catalysis, luminescence studies and medicinal applications, novel approaches were described in the literature, including for example the synthesis of 1D and 3D materials, novel bimetallic complexes endowed with peculiar characteristics, the use as capping agent to stabilise metal nanoparticles (MNPs) and further derivatisations of the adamantyl cage.

In this review article, recent (2010–2017) contributions in the field of synthetic coordination chemistry of PTA and its novel derivatives and use in catalysis will be summarised.

In the field of medicinal inorganic chemistry, the number of reports on the use of ruthenium(II)–arene PTA (RAPTA-type) complexes grew dramatically in the reference years due to their activity as antitumour agents. The synthetic chemistry and the most effective derivatisations of RAPTA complexes, together with studies of the mechanisms of interaction with cells obtained by different experimental techniques and theoretical calculations, has been recently reviewed [2]. Thus, these literature data will not be included in the present review article. The antitumour activity of other classes of PTA complexes will be mentioned in the chapters related to the corresponding syntheses. Finally, the use of (mainly) Group 11 coordination compounds of PTA as antimicrobial agents has recently emerged as a viable application, and selected examples will be here described.

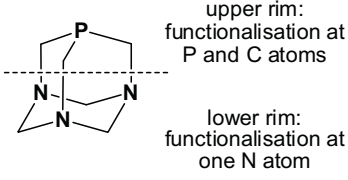


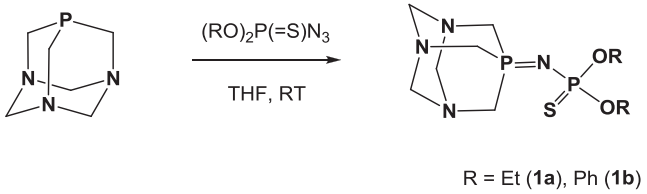
Chart 1. 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane (PTA).

2. Recent ligand structural variations and functionalisations

As previously reviewed [1], PTA can be functionalised either at the "upper rim", on P or C atoms, or at the "lower rim", essentially through quaternisation of a N atom (Chart 1). Whereas the target of C-atom functionalisation is mainly to introduce a pendant arm with donor atoms in such a way to obtain a bidentate P-element ligand, the formation of N—C bonds is generally thought as a suitable way to tune water-solubility and add the desired degree of lipophilicity to the parent compound. Novel PTA analogues and miscellaneous synthetic reactions will be briefly reported below. Table S1 (Supporting Information) summarises ^{1}H and $^{31}P\{^{1}H\}$ NMR data reported in the literature cited, including deuterated solvents used, for the novel ligands and complexes.

2.1. Upper rim functionalisations

P-atom derivatives: Iminophosphorane PTA analogues **1a** and **1b** were obtained by Staudinger-type reaction of PTA with thiophosphoryl azides $(RO)_2P(=S)N_3$ (Scheme 1, R = Et, **1a**; Ph, **1b**) [3]. The products were fully characterised and showed $^{31}P\{^{1}H\}$ NMR doublets with $^{2}J_{PP}$ = 8.9 Hz, at −27.92 ppm for the iminophosphorane and at 62.38 ppm for the thiophosphoryl group in the case of **1a**,



Scheme 1. PTA–iminophosphorane derivatives.