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Short communication

Syntheses and characterisation of novel *N*/*O* trispirocyclic cyclotriphosphazenes as ligands for endotopic metal-binding complexes

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ABSTRACT

Novel *cis*,*trans*,*trans* and *cis*,*cis*,*cis N*/*O* trispirocyclic cyclotriphosphazenes, *ctt*-**4** and all-*cis*-**4**, were synthesised by the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with 2-(1*H*-pyrazol-3-yl)phenol **2** in the presence of base. The reactions of *ctt*-**4** and all-*cis*-**4** with copper(I) iodide afforded binuclear complex **5** and mononuclear complex **6**, respectively. All new cyclotriphosphazenes were characterised by NMR spectroscopy and the complexes **5** and **6** were also characterised by single-crystal X-ray structural analysis.

Cyclotriphosphazenes bearing several substituents capable of coordination to metal have attracted attention as multi-site coordination ligands to give homo- or heteropolynuclear complexes involving identical or different coordination modes [1]. The diversity of coordination modes must result from the flexibility of the coordinating substituents and/or the participation of the phosphazene ring nitrogen in the coordination. Conversely, it is difficult to control the coordination modes of the cyclotriphosphazene complexes. The Lewis basicity of the phosphazene ring nitrogen can be enhanced by the high density of π-electrons on the nitrogen atoms [2], which can be explained with the traditional Lewis ionic structure and Dewar's island model [3]. Thus, the cyclotriphosphazene ring is not required to be planar in contrast with benzene derivatives from the viewpoint of the π-electron distribution. However, most cyclotriphosphazene derivatives assume a planar structure that permits slight deformation depending on the substituent [4] and on whether the P—N bond in the phosphazene ring has multiple bond character [2–5].

The metal-binding sites of the cyclotriphosphazene complexes can be roughly classified into exo- and endotopic sites (Fig. 1), and the endotopic binding complex can potentially show unique photochemical properties attributed to the through-space charge transfer between the phosphazene ring and the metals. Most cyclotriphosphazene complexes whose structures have been confirmed by single-crystal X-ray structural analysis, have exotopic metal-binding sites [1,6–7]. In contrast, the cyclotriphosphazene ligands with endotopic metal-binding sites were confined to those with polyanionic character [8] or distant binding sites from the phosphazene ring [9], and these could also provide exotopic metal-binding sites. It is notable that endotopic metal-binding complexes were also synthesised from cyclotriphosphazene bearing no coordinating substituents by template methods with dilithiometallocenes [10]. To the best of our knowledge, there have been no reports on the cyclotriphosphazene ligands providing only endotopic metal-binding sites, although the potential for a stacked metal complex of tris(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene has been proposed [11].

Cyclotriphosphazenes bearing several pyrazolyl groups have been used successfully as ligands for a wide variety of stable exotopic metal-binding complexes [1,6]. The pyrazolyl groups in such ligands are allowed to rotate around the P—N bond. However, there have been no attempts to direct the nitrogen lone pair of the pyrazolyl group toward only endotopic metal-binding sites by embedding the pyrazolyl group in the spiro framework of a spirocyclic cyclotriphosphazene. The *N*/*O* bifunctional reagents have been useful for the syntheses of stable spirocyclic cyclotriphosphazenes [9c,12]. We envisioned that the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with 2-(1*H*-pyrazol-3-yl)phenol **2** could generate a ligand to afford an only endotopic metal-binding complex. Herein, we report on the syntheses and characterisation of novel *N*/*O* trispirocyclic cyclotriphosphazenes *cis*,*trans*,*trans*(*ctt*)- and *cis*,*cis*,*cis*(all-*cis*)-**4**, in

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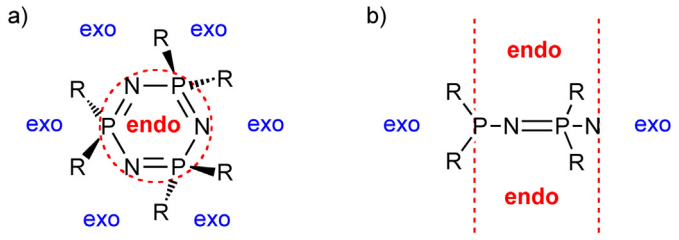


Fig. 1. Classification of the metal-binding sites of the cyclotriphosphazene complexes. a) Top view. b) Side view.

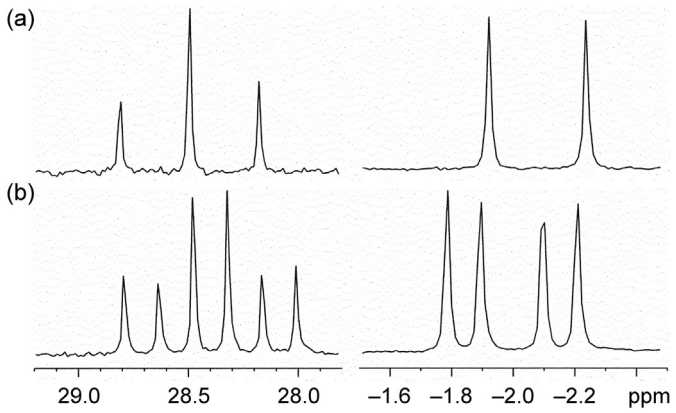


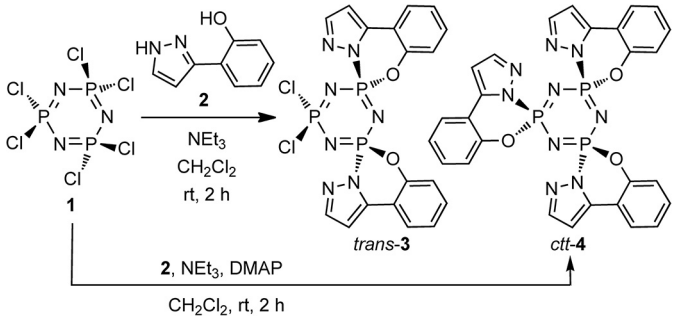
Fig. 2. $^{31}P\{^1H\}$ NMR (243 MHz) spectra of *trans*-**3** in $CDCl_3$. (a) before the addition of CSA. (b) after addition of CSA at ca. 10:1 M ratio.

which the pyrazolyl groups were embedded in the spiro frameworks, and their configurational confirmation by single-crystal X-ray structural analysis of their copper(I) complexes **5** and **6**, respectively.

In the presence of 9 equiv. of triethylamine as an HCl scavenger, the reaction of $N_3P_3Cl_6$ (**1**) with 3 equiv. of 2-(1*H*-pyrazol-3-yl)phenol **2** in CH_2Cl_2 afforded *trans N/O* dispirocyclic cyclotriphosphazene *trans*-**3** and *cis,trans,trans N/O* trispirocyclic cyclotriphosphazene *ctt*-**4** as white powders in 63% and 29% yields, respectively (Scheme 1). By the addition of 1 equiv. of 4-(dimethylamino)pyridine (DMAP) as a nucleophilic catalyst, *ctt*-**4** could be generated exclusively and isolated in 47% yield. Interestingly, in these reactions, neither the *cis* dispirocyclic isomer nor the all-*cis* trispirocyclic isomer could be obtained by the purification with silica gel chromatography.

The *trans N/O* dispirocyclic cyclotriphosphazene (*trans*-**3**) with C_2 symmetry is chiral, while the *cis* dispirocyclic isomer and *ctt N/O* trispirocyclic cyclotriphosphazene (*ctt*-**4**) with S_1 symmetry and the all-*cis* trispirocyclic isomer (all-*cis*-**4**) with C_{3v} symmetry are achiral. The *trans* configuration and racemate of the dispirocyclic phosphazene *trans*-**3** was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy with (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol as a chiral solvating agent (CSA) [9c,12a–f,13], where splitting of the ^{31}P NMR signals for *trans*-**3** was observed on addition of the CSA in a 10:1 M ratio (Fig. 2). The spin systems in the $^{31}P\{^1H\}$ NMR spectra of *cis,trans,trans* trispirocyclic cyclotriphosphazenes, in which all of the *N/O* substituents are identical, should be interpreted as AB_2 [12c,d]. However, the $^{31}P\{^1H\}$ NMR spectrum of *ctt*-**4** (Fig. 3A-a) exhibits a singlet-like signal at δ 2.0 ppm that is assignable to the all-*cis* isomer. Meanwhile, in the ^1H NMR spectrum, three of six protons in the *N/O* substituent are observed as two separate resonances with a 2:1 integrated intensity ratio (Fig. 3B-a).

The configuration of *ctt*-**4** could be affirmed by the single-crystal X-ray structural analysis of binuclear copper(I) complex **5** with a benzene molecule (Fig. 4), which was obtained as yellow plates by the reaction of *ctt*-**4** with copper(I) iodide in CH_2Cl_2 (Scheme 2) in 40% yield upon recrystallisation of the crude products from benzene. It is found that the arrangement of the phosphazene units is *cis* and the coordination



Scheme 1. Synthesis of cyclotriphosphazenes *trans*-**3** and *cis,trans,trans*-**4**.

modes of the phosphazene ligands are different. The Cu atoms are not located above the centre of the phosphazene ring in the binding phosphazene and one copper atom (Cu1) binds to the endotopic site but the other (Cu2) binds to the exotopic site (Fig. 4b). The difference in the binding sites is probably due to the steric demands between two non-chelate *N/O* substituents, which are recognised by a clear difference in the distances of the O1 and O4 atoms from the I2 atom. The steric effect is also reflected in the longer mean Cu–μI bond length (2.708 Å) in **5** compared to those (2.583–2.637 Å) found in the known binuclear copper(I) complexes with bidentate chelating bis(pyrazole) ligands [14]. In the ^{31}P and ^1H NMR spectra of complex **5** (Fig. 3A,B-b), all the resonances were separated with a 2:1 integrated intensity ratio because the magnetic environments of the *N/O* substituents in complex **5** are less equivalent than those in *ctt*-**4** due to the bidentate binding to the copper(I) atom of the *cis* arranged pyrazolyl groups.

The stereoselectivities in the nucleophilic substitution reactions of cyclotriphosphazenes have been well researched [12d,15–18]. The steric demand of the substituents should favour a *trans* configuration [12d,15,16], and the exclusive *trans* selectivity for the *trans* dispirocyclic phosphazene **3** to give *ctt*-**4** (Scheme 1) may be rationalised by a substituent-solvating effect shown in the reaction with amines as the HCl scavenger and/or nucleophile [15,17]. Subsequently, we investigated the reaction with NaH as the base, in which the nucleophile could be directed *cis* to the oxygen atom of the alkoxy substituents on the phosphorus by coordination of the sodium cation to the oxygen [15,18]. The reaction of **1** with 3 equiv. of the dianion generated by the treatment of **2** with a stoichiometric amount of NaH in THF could afford all-*cis*-**4** as a white powder in low yield (8%), although *trans*-**3** and *ctt*-**4** were also obtained in 12% and 36% yields, respectively (Scheme 3). The polarity of the *cis* isomer is generally high compared with that of the *trans* isomer. Thus, the R_f value (0.20) of all-*cis*-**4** in the silica gel chromatography (CH_2Cl_2/Et_2O 8:1) was significantly smaller than that (0.57) of *ctt*-**4**. Additionally, all-*cis*-**4** was soluble in polar aprotic organic solvents such as CH_2Cl_2, $CHCl_3$, and THF in contrast to *ctt*-**4**, which was less soluble in any organic solvent. The C_{3v}-symmetric structure of all-*cis*-**4** was revealed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, showing six signals (Fig. 3B-c), and a clear singlet resonance appeared at δ 1.9 ppm (Fig. 3A-c), which was nearly identical to the ^{31}P chemical shift of *ctt*-**4** (δ 2.0 ppm).

The configuration of all-*cis*-**4** could also be affirmed by single-crystal X-ray structural analysis of mononuclear copper(I) complex **6** with three 1,2-dichloroethane (DCE) molecules (Fig. 5), which was obtained as orange prisms by the reaction of all-*cis*-**4** with copper(I) iodide in CH_2Cl_2 (Scheme 4) in 65% yield upon recrystallisation of the crude products from DCE. It is found that the complex **6** is a mononuclear