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EFFICIENT SYNTHESIS OF CYCLOTRIPHOSPHAZENE TRIPODAL TRIDENTATE LIGAND VIA THE COPPER(I)-TEMPLATE METHOD

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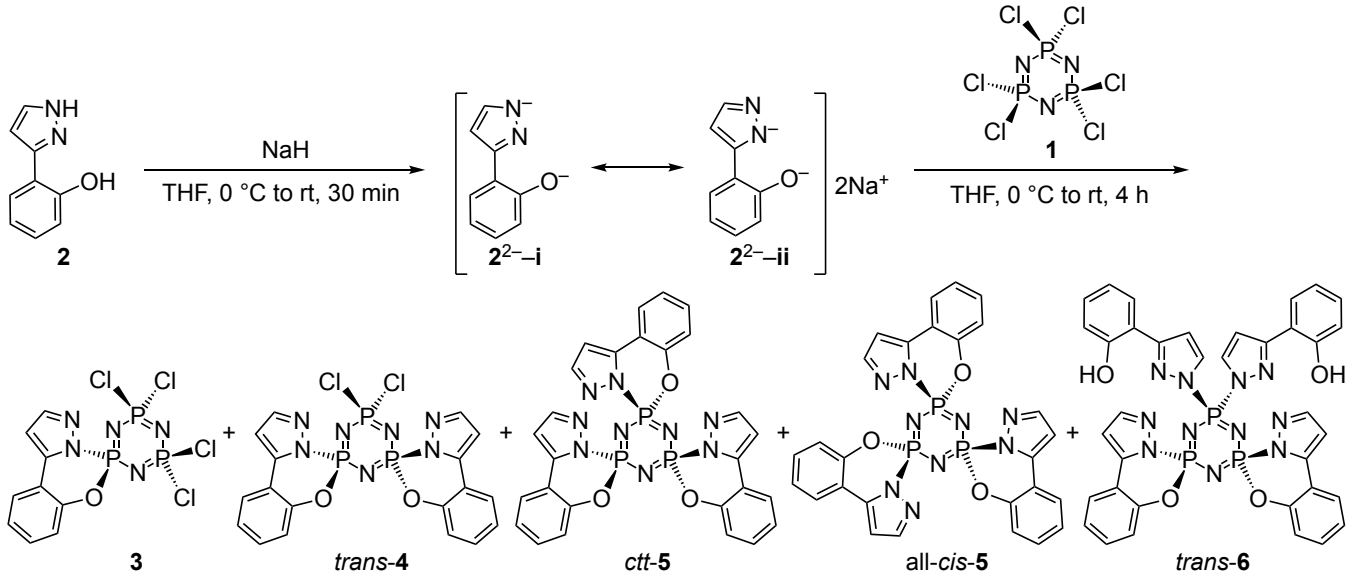
Abstract – An efficient synthesis of a cyclotriphosphazene tripodal tridentate ligand, *cis*,*cis*,*cis*-*N*/*O* trispirocyclic cyclotriphosphazene, via the copper(I)-template method was described. The reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with 3 equiv of the dianion generated from 2-(1*H*-pyrazol-3-yl)phenol and NaH in THF in the presence of CuI afforded a copper(I) complex of the cyclotriphosphazene ligand in 51% yield. The solution of the complex in CH_2Cl_2 was treated with 25% NH_3 aqueous solution to give the ligand in 82% yield. The 42% overall yield of the ligand via the complex starting from $N_3P_3Cl_6$ was adequately improved compared to the yield of 8% in the reported synthesis of the ligand in the absence of CuI.

Cyclotriphosphazene consists alternate phosphorus and nitrogen atoms in its six-membered ring core, in which the geometry of the phosphorus atom is a tetrahedral structure. Nucleophilic substitution reactions at the phosphorus atoms of cyclotriphosphazenes have attracted attention because of their regio- and stereochemically diverse pathways.[1] In the reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with *N*/*O* bifunctional reagents to give dispiro-[2,3] and trispirocyclic[3] cyclotriphosphazenes, *trans*/*cis* and *cis*,*trans*,*trans*(*ctt*)/*cis*,*cis*,*cis*(all-*cis*) selectivities, respectively, can be mainly accounted for by the steric demand of the substituents,[1b,2d,e3d] the substituent-solvating effect,[1b,3c,4] and the *cis*-directing effect of the sodium cation coordinated by the oxygen lone pairs of an exocyclic P–O moiety.[1b,5]

Cyclotriphosphazenes bearing functional groups capable of coordination to metal have also attracted attention as the polydentate ligands to give the complexes with various coordination modes.[6] Among the cyclotriphosphazene complexes, the endotopic metal-binding complexes both in crystal or in solution have been confined to polyanionic phosphazenate[7] or metallocene derivatives.[8] Additionally, no

cyclotriphosphazene ligand providing only endotopic metal-binding site has been synthesized, although the potential for a stacked metal complex of cyclotriphosphazene has been proposed.[9]

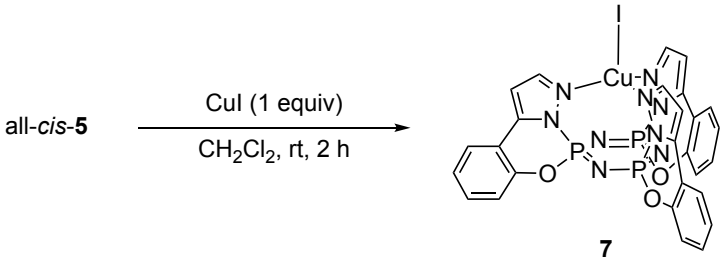
Table 1. Effect of molar ratio of 2-(1*H*-pyrazol-3-yl)phenol (**2**) with $N_3P_3Cl_6$ (**1**) on product selectivity



Entry	**1**/**2** molar ratio[a]	Yield (%)[b]				
		3	*trans*-**4**	*ctt*-**5**	all-*cis*-**5**	*trans*-**6**
1	1:1	68	0	0	0	0
2	1:2	7	65	0	0	0
3	1:3[10]	0	12	36	8	0
4	1:4	0	0	39	6	8

[a] **2**/NaH molar ratio 1:2. [b] Isolated yield.

Recently, we have reported on the synthesis of *N*/*O* spirocyclic cyclotriphosphazenes involving pyrazolyl groups embedded in the spirocyclic frameworks by the reaction of **1** with three equiv of 2-(1*H*-pyrazol-3-yl)phenol (**2**) in the presence of base, in which all-*cis*-**5** was obtained in low yield (8%) with *trans*-**4** (12%) and *ctt*-**5** (36%) by using NaH as base in THF (Table 1, entry 3).[10] Then the reaction of all-*cis*-**5** with CuI in CH_2Cl_2 afforded a copper(I) complex **7** with three 1,2-dichloroethane (DCE) molecules in 65% yield upon recrystallization of the crude products from DCE (Scheme 1).[10]



Scheme 1. Synthesis of copper(I) complex **7**

All-*cis*-**5** is the first example of the cyclotriphosphazene ligand providing only endotopic metal-binding site and also a new class of tripodal tridentate ligands represented by scorpionates[11] because of its preferentially tridentate character and expanded coordination pocket that arise from the rigidity of spirocyclic frameworks and large backbone structure containing the cyclotriphosphazene ring, respectively. In our continuous effort to develop the method for the synthesis of all-*cis*-**5**, here we present an efficient synthesis of all-*cis*-**5** via the copper(I)-template method.

As part of the screening of reaction conditions for the synthesis of all-*cis*-**5** by using NaH as base in THF, the reaction of **1** using one, two, and three equiv of **2** afforded spirocyclic (**3**), dispirocyclic (*trans*-**4**), and trispirocyclic (*ctt*-**5**) cyclotriphosphazenes, respectively, as major products (Table 1, entry 1–3). However, when using four equiv of **2**, the sum of the yields of trispirocyclic products *ctt*-**5** and all-*cis*-**5** did not increase and a small amount of the *trans*-dispirocyclic cyclotriphosphazene *trans*-**6** involving four pyrazolyl groups was isolated (Table 1, entry 4).

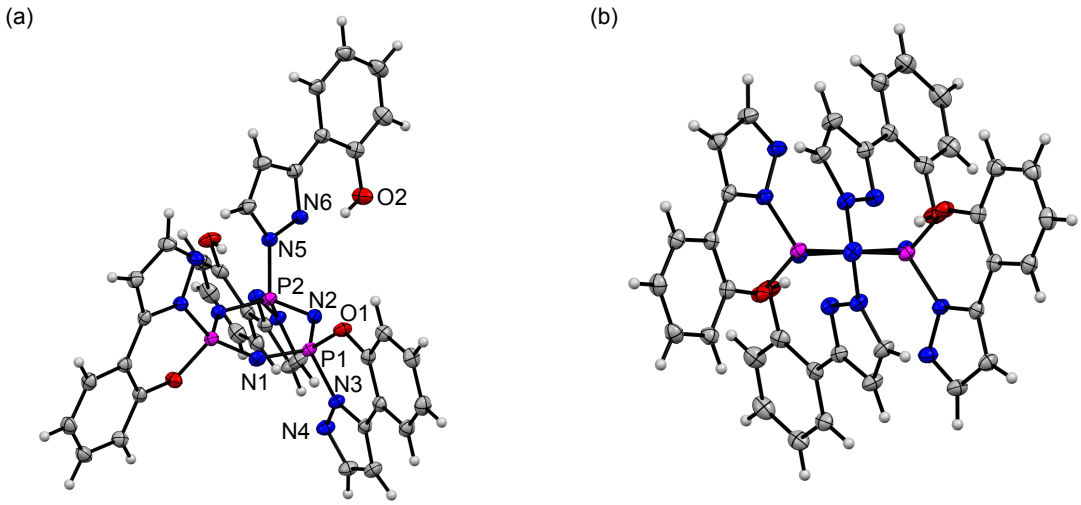


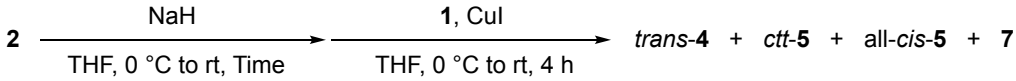
Figure 1. The ORTEP drawing of *trans*-**6** showing the thermal ellipsoids at the 50% probability level. (a) Over view. (b) Side view.

Colorless plates of *trans*-**6** were grown by recrystallization from dichloroethane, which crystallized in the monoclinic space group *I*2/*a*.[12] As shown in ORTEP drawing of *trans*-**6** (Figure 1), two geminal pyrazolyl

groups connected at the 1-position in 2-(1*H*-pyrazol-3-yl)phenol to phosphorus, which could not allow the formation of spirocyclic framework. This implies that the nucleophilic attack of a dianion $\mathbf{2}^{2-}$–**i** at the phosphorus atoms might hamper the formation of the *cis*-dispirocyclic and all-*cis*-trispirocyclic isomers resulting from the *cis*-directing effect of the sodium cation.[1b,5] Therefore, we aimed to synthesize the complex **7** using copper(I)-template method, in which the nitrogen atoms at 1-position in 2-(1*H*-pyrazol-3-yl)phenol coordinated to the copper atom.

Under the reaction condition to provide the best yield of all-*cis*-**5** (Table 1, entry 3), the reaction of **1** with the dianion of **2** was carried out in the presence of one equiv of CuI and the reaction mixture was purified by silica gel chromatography to give the complex **7** in low yield (23%) with *trans*-**4** and *ctt*-**5** (Table 2, entry 1). Interestingly, the shorter reaction time for the treatment of **2** with NaH could lead to an improvement of the yield (51%) of **7** (Table 2, entry 2). Some degradation products of the dianion of **2** might prevent the formation of the spirocyclic cyclotriphosphazenes while there were reports on the treatment performed for a longer time.[13] In these reactions, the *cis* isomer of *trans*-**4** and the corresponding copper(I) complex could not be obtained, which suggests that they are transient species to give the trispirocyclic cyclotriphosphazenes.

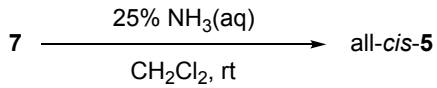
Table 2. The synthesis of the complex **7** using copper(I)-template method



Entry	Time (min)	**1**/**2** molar ratio[a]	Yield (%)[b]			
			trans-**4**	*ctt*-**5**	all-*cis*-**5**	**7**
1	30	1:3	22	11	0	23
2	10	1:3	12	8	0	51

[a] **2**/NaH molar ratio 1:2. [b] Isolated yield.

Demetallation of the copper(I) complex **7** could be achieved by the treatment of the solution of **7** in CH_2Cl_2 with 25% NH_3 aqueous solution[14] to give all-*cis*-**5** in high yield (82%). The overall yield (42%) of all-*cis*-**5** via **7** starting from **1** was higher than that (8%) of the reaction of **1** with the dianion of **2** in the absence of CuI (Table 1, entry 3).



Scheme 2. Demetallation of the copper(I) complex **7**

In conclusion, the reaction of $N_3P_3Cl_6$ (**1**) using one, two, and three equiv of the dianion generated from 2-(1*H*-pyrazol-3-yl)phenol (**2**) and NaH afforded spirocyclic (**3**), dispirocyclic (*trans*-**4**), and trispirocyclic (*ctt*-**5**) cyclotriphosphazenes, respectively, as major products. When using four equiv of **2**, the sum of the yields of trispirocyclic products *ctt*-**5** and all-*cis*-**5** did not increase and the *trans*-dispirocyclic cyclotriphosphazene *trans*-**6** involving four pyrazolyl groups was also isolated. The copper(I) complex **7** of the tripodal tridentate ligand all-*cis*-**5** could be obtained in 51% yield by the reaction of **1** using 3 equiv of **2** in the presence of CuI. The treatment of the solution of the complex **7** in CH_2Cl_2 with 25% NH_3 aqueous solution gave the ligand all-*cis*-**5** in 82% yield. The 42% overall yield of all-*cis*-**5** via the complex **7** starting from **1** was adequately improved compared to the yield of 8% in the reported synthesis of all-*cis*-**5** in the absence of CuI.[10]

EXPERIMENTAL

General. All reactions were carried out under an atmosphere of nitrogen. All reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. THF was freshly distilled from Na-benzophenone under an atmosphere of nitrogen. Column chromatography was performed under air using Silica Gel 60N (Kanto Chemical Co., Inc., 0.063–0.210 mm).

Melting points were measured with a Yanaco micro melting point system MP-S3 and were uncorrected. ^{1}H (600 MHz), ^{13}C (151 MHz), and ^{31}P (243 MHz) NMR spectra were recorded on a Bruker AVANCE-II (600 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts (δ) are given in ppm downfield from internal Me_4Si or from residual chloroform (δ = 7.26 and 77.0 for ^{1}H and ^{13}C NMR, respectively). ^{31}P NMR chemical shifts (δ) are given in ppm downfield from external 85% H_3PO_4. Some ^{13}C NMR signals appear as multiplets and second-order deceptive triplets.[15] Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Typical procedure for the reaction of $N_3P_3Cl_6$ (1) with the dianion of 2-(1*H*-pyrazol-3-yl)phenol (2): 2,2,4,4-Tetrachloro-6,6-[2-(1*H*-pyrazol-5-yl)phenoxy]cyclotriphosphazene (3)

To a solution of **2** (1.84 g, 11.5 mmol) in 45 mL of THF was added dropwise a suspension of NaH (55% dispersion in paraffin liquid, 1.01 g, 23.1 mmol) in 120 mL of THF at 0 °C and the solution was stirred for 30 min at room temperature. The solution was then added to a solution of **1** (4.00 g, 11.5 mmol) in 250 mL of THF at 0 °C and the reaction mixture was stirred for 4 h at room temperature. Then the reaction mixture was quenched with H_2O (350 mL) and extracted with CH_2Cl_2 (500 mL x 4). The collected organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography with CH_2Cl_2-Et_2O (8:1) as eluent to give **3** (3.42 g, 68%) as white powder. R_f = 0.96; mp 209 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98 (dd, J = 4.2, 1.8 Hz, 1H), 7.69 (ddd. J = 7.2, 2.1, 0.6 Hz, 1H), 7.41 (ddt, J = 8.4, 7.2, 1.8 Hz, 1H),

7.31–7.29 (m, 2H), 6.75 (dd, J = 3.6, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 147.9 (d, J = 8.8 Hz), 146.8 (d, J = 18.7 Hz), 143.2 (d, J = 10.3 Hz), 130.8, 125.6 125.3, 119.2 (d, J = 10.1 Hz), 115.1 (d, J = 4.2 Hz), 103.1 (d, J = 5.3 Hz); ^{31}P NMR ($CDCl_3$, 243 MHz) δ 24.7 (d, J = 68.0 Hz, 2P), –7.1 (t, J = 68.0 Hz, 1P); Anal. Calcd for $C_9H_6N_5Cl_4OP_3$: C 24.86, H 1.39, N 16.10. Found: C 24.61, H 1.06, N 15.73.

***Trans*-2,2-dichloro-4,4,6,6-bis[2-(1*H*-pyrazol-5-yl)phenoxy]cyclotriphosphazene (*trans*-4)**

According to the typical procedure for the reaction of $N_3P_3Cl_6$ (**1**) with the dianion of 2-(1*H*-pyrazol-3-yl)phenol (**2**), *trans*-**4** (3.88 g, 65%) was obtained as white powder together with **3** (0.332 g, 7%) using **2** (3.68 g, 23.0 mmol) and NaH (55% dispersion in paraffin liquid, 2.01 g, 46.1 mmol). R_f = 0.83; mp 265 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.03 (dd, J = 3.6, 1.8 Hz, 2H), 7.66 (ddd, J = 7.8, 1.8, 0.6 Hz, 2H), 7.40–7.37 (m, 2H), 7.35 (dd, J = 7.8, 1.8 Hz, 2H), 7.25 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 6.75 (dd, J = 3.6, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.2, 146.7 (t, J = 18.7 Hz), 143.5, 130.8, 125.4, 125.3, 119.6 (t, J = 10.6 Hz), 115.4, 103.0; ^{31}P NMR ($CDCl_3$, 243 MHz) δ 28.5 (t, J = 77.8 Hz, 1P), –2.1 (d, J = 77.8 Hz, 2P); Anal. Calcd for $C_{18}H_{12}N_7Cl_2O_2P_3$: C 41.40, H 2.32, N 18.78. Found: C 41.05, H 2.16, N 18.46.

***trans*-2,2-Bis[3-(2-hydroxyphenyl)-1*H*-pyrazolyl]-4,4,6,6-bis[2-(1*H*-pyrazol-5-yl)phenoxy]cyclotriphosphazene (*trans*-6)**

According to the typical procedure for the reaction of $N_3P_3Cl_6$ (**1**) with the dianion of 2-(1*H*-pyrazol-3-yl)phenol (**2**), *trans*-**6** (0.700 g, 8%) was obtained as white powder together with *ctt*-**5** (white powder, 2.70 g, 39%) and all-*cis*-**5** (white powder, 0.446 g, 6%) using **2** (7.36 g, 46.0 mmol) and NaH (55% dispersion in paraffin liquid, 4.02 g, 92.1 mmol). R_f = 0.95; mp 235 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.03 (s, 2H), 8.41 (dd, J = 3.0, 0.6 Hz, 2H), 8.04 (dd, J = 3.6, 1.8 Hz, 2H), 7.67 (dd, J = 7.8, 1.2 Hz, 2H), 7.56 (dd, J = 7.8, 1.8 Hz, 2H), 7.34 (t, J = 8.4 Hz, 2H), 7.29 (dd, J = 8.4, 0.6 Hz, 2H), 7.24 (dt, J = 7.2, 1.2 Hz, 2H), 7.20 (ddd, J = 8.4, 7.2, 1.8 Hz, 2H), 6.91–6.87 (m, 6H), 6.78 (dd, J = 3.0, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 158.3 (d, J = 13.9 Hz), 156.4, 148.2 (t, J = 7.7 Hz), 146.4 (t, J = 17.7 Hz), 143.4 (t, J = 9.4 Hz), 136.7 (d, J = 11.8 Hz), 130.7, 130.5, 127.4, 125.2, 125.1, 119.5 (t, J = 9.2 Hz), 119.2, 117.3, 115.4, 115.3, 106.0 (d, J = 6.5 Hz), 102.8; ^{31}P NMR ($CDCl_3$, 243 MHz) δ 1.92 (dd, J = 94.8, 60.8 Hz, 1P), 1.12 (d, J = 60.8 Hz, 1P), 1.08 (d, J = 94.8, 1P); Anal. Calcd for $C_{36}H_{26}N_{11}O_4P_3$: C 56.18, H 3.41, N 20.02. Found: C 56.28, H 3.08, N 20.26.

***cis-trans-trans*-2,2,4,4,6,6-Tris[2-(1*H*-pyrazol-5-yl)phenoxy]cyclotriphosphazene (*ctt*-5)**

R_f = 0.57; mp 221 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, J = 1.2 Hz, 3H), 7.62 (dd, J = 7.8, 1.8 Hz, 1H), 7.61 (dd, J = 7.8, 1.2 Hz, 2H), 7.42 (dd, J = 8.4, 0.6 Hz, 1H), 7.37 (dd, J = 8.4, 1.2 Hz, 2H), 7.34 (dd, J = 8.4, 7.2 Hz, 3H), 7.20 (d, J = 7.8, 1.2 Hz, 3H), 6.72 (q, J = 1.2 Hz, 1H), 7.70 (d, J = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.5–148.4 (m), 148.3, 148.2, 146.9–146.7 (m), 146.5–146.3, 143.5–143.4 (m), 130.7, 130.5, 130.4, 125.2, 125.1, 125.1, 119.8 (d, J = 4.8 Hz), 119.6, 119.4, 115.7, 115.6, 115.4,

102.8, 102.7; ^{31}P NMR ($CDCl_3$, 243 MHz) δ 2.0; Anal. Calcd for $C_{27}H_{18}N_9O_3P_3$: C 53.21, H 2.98, N 20.69. Found: C 53.03, H 2.98, N 20.22.

***cis*-*cis*-*cis*-2,2,4,4,6,6-Tris[2-(1*H*-pyrazol-5-yl)phenoxy]cyclotriphosphazene (all-*cis*-5)**

R_f = 0.20; mp 219 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.07 (d, J = 1.2 Hz, 3H), 7.60 (dd, J = 7.8, 1.2 Hz, 3H), 7.36 (dd, J = 7.8, 1.8 Hz, 3H), 7.33 (ddd, J = 8.4, 7.2, 1.2 Hz, 3H), 7.19 (ddd, J = 8.4, 6.6, 1.2 Hz, 3H), 6.68 (q, J = 1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 148.3 –148.2 (m), 146.9–146.7 (m), 143.4 (d, J = 11.0 Hz), 130.4, 125.2, 125.1, 119.43–119.37 (m), 115.8, 102.9; ^{31}P NMR ($CDCl_3$, 243 MHz) δ 1.9; Anal. Calcd for $C_{27}H_{18}N_9O_3P_3$: C 53.21, H 2.98, N 20.69. Found: C 52.88, H 2.88, N 20.91.

Template synthesis of iodo[*cis*-*cis*-*cis*-2,2,4,4,6,6-tris[2-(1*H*-pyrazol-5-yl)phenoxy-κN^2]cyclotriphosphazene]copper(I) (7)

To a solution of **2** (5.52 g, 34.5 mmol) in 45 mL of THF was added dropwise a suspension of NaH (55% dispersion in paraffin liquid, 3.01 g, 69.0 mmol) in 120 mL of THF at 0 °C and the solution was stirred for 10 min at room temperature. The solution was then added to a solution of **1** (4.00 g, 11.5 mmol) and CuI (2.19 g, 11.5 mmol) in 250 mL of THF at 0 °C and the reaction mixture was stirred for 4 h at room temperature. Then the reaction mixture was quenched with H_2O (350 mL) and extracted with CH_2Cl_2 (1000 mL x 3). The collected organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography with CH_2Cl_2-Et_2O (8:1) as eluent to give **7** (4.68 g, 51%) as yellow powder together with *trans*-**4** (0.747 g, 12%) and *ctt*-**5** (0.586 g, 8%). R_f = 0.78; mp 242 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.92 (s, 3H), 7.68 (dd, J = 7.8, 1.8 Hz, 3H), 7.43 (t, J = 7.8 Hz, 3H), 7.33 (dd, J = 8.4, 1.2 Hz, 3H), 7.28 (dt, J = 7.8, 1.2 Hz, 3H), 6.75 (d, J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 149.8–149.7 (m), 148.1, 143.1–143.0 (m), 131.4, 125.8, 125.7, 119.2–119.1 (m), 114.9, 102.7; ^{31}P NMR ($CDCl_3$, 243 MHz) δ 0.4; Anal. Calcd for $C_{27}H_{18}N_9CuIO_3P_3$: C 40.54, H 2.27, N 15.76. Found: C 40.76, H 1.88, N 15.45.

Demetallation of the copper(I) complex 7

A solution of the copper(I) complex **7** (4.68 g, 5.85 mmol) in 500 mL of CH_2Cl_2 was treated in a separatory funnel with 25% NH_3 aqueous solution (100 mL x 3). The organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. Purification of the residue was carried out by silica gel column chromatography with CH_2Cl_2-Et_2O (8:1) as eluent to give all-*cis*-**5** (2.93 g, 82%) as white powder.

Single-crystal X-ray structural analysis

The diffraction data were measured on an XtaLAB Synergy-S, Dualflex, HyPix diffractometer using Cu-*K*α radiation (λ = 1.54184 Å) at 120 K. The data collection and processing were carried out with CrysAlis^{Pro} software. The structure was solved by direct method using SHELXT. All non-hydrogen atoms were refined anisotropically. The hydrogen atom directly attached to O2 was located from a difference

Fourier map calculated at a late stage of the structural analysis. All other hydrogen atoms were refined using a riding model.

Crystal data: $C_{36}H_{26}N_{11}O_4P_3$, M = 769.59, monoclinic, $I2/a$ (No. 15), a = 12.1318(2) Å, b = 14.2037(2) Å, c = 20.9205(3) Å, β = 104.155(2)°, V = 3495.49(10) Å^3, Z = 4, D_{calcd} = 1.462 g cm^{-3}, μ(Cu-Ka) = 2.061 mm^{-1}, F(000) = 1584.0, 12092 reflections collected, 3518 unique (R_{int} = 0.0238), 249 parameters, R_1 = 0.0315 ($I > 2\sigma(I)$), wR_2 = 0.0865 (all data), GOF = 1.069.

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