SYNTHESIS AND STRUCTURES OF ALKYNYLCHLOROCYCLOTRIPHOSPHAZENES AND THEIR CLUSTER-FORMING REACTIONS WITH OCTACARBONYLDICOBALT[†]

Takashi Komuro, Kenichi Mori, and Hiromi Tobita*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan. E-mail: tobita@m.tains.tohoku.ac.jp

[†] Dedication to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday

Abstract − Cyclotriphosphazenes having *p*-tolylethynyl and chloro substituents $N_3P_3\{C\equiv C(p\text{-Tol})\}_nCl_{6-n}$ (**1a**: $n = 2$, **1b**: $n = 4$; *p*-Tol = *p*-tolyl) were synthesized by the reaction of hexachlorocyclotriphosphazene $(NPCl_2)_3$ with 2 equiv of $LiC\equiv C(p\text{-Tol})$ in THF. **1a** and **1b** were characterized by spectroscopic methods and elemental analyses. The reactions of **1a** and **1b** with octacarbonyldicobalt $Co_2(CO)_8$ produced cobalt clusters containing tetrahedral $C_2Co_2(CO)_6(p\text{-Tol})$ cluster units; namely, tetranuclear cluster $N_3P_3\{C_2Co_2(CO)_6(p\text{-Tol})\}_2Cl_4$ (**2**) and hexanuclear cluster $N_3P_3\{C_2Co_2(CO)_6(p\text{-Tol})\}_3\{C\equiv C(p\text{-Tol})\}Cl_2$ (**3**). Crystal structures of **1a** and **2** were determined by X-ray crystallography.

INTRODUCTION

Functionalized cyclotriphosphazenes are attractive for their application to a multi-site-coordination ligand in coordination and organometallic chemistry.[1] Cyclotriphosphazenes $(NPX_2)_3$ have six exocyclic substituents X on the three phosphorus atoms (Chart 1) and can be tailored by functionalization of the substituents X with coordinating groups to construct multi-site-coordination ligands. For example, cyclotriphosphazene ligands having N-donor substituents such as pyrazolyl, pyridyloxy, and amino groups have been extensively investigated in coordination chemistry of transition metals.[1] One of the unique features of the cyclotriphosphazene ligands is their potential utility as bridging ligands for the synthesis of multinuclear metal complexes.

Since an alkynyl group acts as a ligand to form organometallic complexes by coordination of the C≡C bond to transition metals, we have aimed at the synthesis of cyclotriphosphazenes having plural alkynyl

groups. Although the synthesis of several alkynyl-substituted cyclotriphosphazenes[2–5] and their reactivity toward cobalt and iron complexes[2,5–9] have been investigated, cyclotriphosphazenes having more than two alkynyl substituents have not yet been synthesized. To prepare cyclotriphosphazenes having different numbers of alkynyl groups, we have used a salt elimination reaction between hexachlorocyclotriphosphazene $(NPCl_2)_3$ and alkynyllithium. As the closely related works, Chivers[2] and Allen *et al*.[4,5] have reported the reactions of hexafluorocyclotriphosphazene $(NPF_2)_3$ with alkynyllithium reagents $LiC{\equiv}CR$ (R = Ph, SiMe_3, Me, *n*-Bu) giving mono- and disubstituted alkynylfluorocyclotriphosphazenes $N_3P_3(C{\equiv}CR)_nF_{6-n}$ ($n = 1, 2$). Hexachlorocyclotriphosphazene $(NPCl_2)_3$ is thought to be a more convenient starting material compared to the fluoride analog $(NPF_2)_3$, since the latter is a volatile liquid and is usually derived from $(NPCl_2)_3$.[10] However, to the best of our knowledge, the reaction of $(NPCl_2)_3$ with alkynyllithium has not been used for P–C(alkynyl) bond formation,[11] probably because the reaction of $(NPCl_2)_3$ with organolithium reagents usually results in a complicated mixture accompanied by the ring cleavage of the cyclotriphosphazene moiety.[2,12] Herein, we describe the synthesis of alkynylchlorocyclotriphosphazenes having two or four *p*-tolylethynyl groups by the reaction between $(NPCl_2)_3$ and *p*-tolylethynyllithium. We also describe the reactions of the alkynylchlorocyclotriphosphazenes with octacarbonyldicobalt that give tetra- and hexanuclear cobalt clusters.
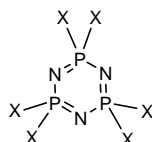

Chart 1. Cyclotriphosphazenes $(NPX_2)_3$ (X = various substituents).

RESULTS AND DISCUSSION

Preparation of alkynylchlorocyclotriphosphazenes 1a and 1b

Treatment of hexachlorocyclotriphosphazene $(NPCl_2)_3$ with 2 equiv of $LiC{\equiv}C(\textit{p}\text{-Tol})$ in THF gave a mixture containing bis(*p*-tolylethynyl)tetrachlorocyclotriphosphazene $N_3P_3\{C{\equiv}C(\textit{p}\text{-Tol})\}_2Cl_4$ (**1a**) and tetrakis(*p*-tolylethynyl)dichlorocyclotriphosphazene $N_3P_3\{C{\equiv}C(\textit{p}\text{-Tol})\}_4Cl_2$ (**1b**) in ca. 6 : 1 molar ratio (eq. 1).[13] Compounds **1a** and **1b** in the mixture were separated by silica gel flash chromatography[14] and isolated in 54 and 5% yields, respectively. **1a** and **1b** are both one of the geminal isomers, which contain only $P\{C{\equiv}C(\textit{p}\text{-Tol})\}_2$ and PCl_2 moieties but no $P\{C{\equiv}C(\textit{p}\text{-Tol})\}Cl$ moieties.[15,16] In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, no signals were observed for cyclotriphosphazenes having a $P\{C{\equiv}C(\textit{p}\text{-Tol})\}Cl$ moiety, i.e., non-geminal isomers of **1a** and **1b** as well as mono- or trisubstituted cyclotriphosphazenes (vide infra). It has been reported that the reaction of $(NPF_2)_3$ with 2 equiv of $LiC{\equiv}CPh$ in diethylether afforded the geminal isomer of

bis(phenylethynyl)tetrafluorocyclotriphosphazene $N_3P_3(C\equiv CPh)_2F_4$ almost selectively,[2,4] but, in this case, formation of a small amount of non-geminal isomers was also observed.[4]
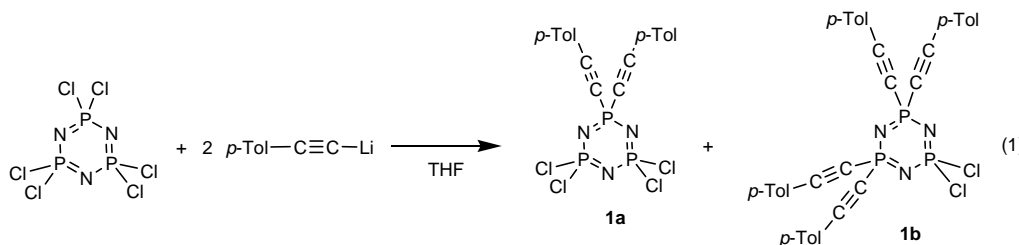
Compounds **1a** and **1b** were characterized by spectoroscopic methods (NMR, IR, and MS) and elemental analyses. In the ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, **1a** and **1b** show only one set of the signals for the *p*-tolylethynyl groups. This indicates that all the *p*-tolyl groups in **1a** and also in **1b** are equivalent. The $^{31}P\{^1H\}$ NMR spectrum of **1a** exhibits a doublet and a triplet signal. The doublet signal appears at 19.3 ppm and, since the chemical shift is comparable to that of $(NPCl_2)_3$ (20.5 ppm), it is assignable to the chloro-substituted phosphorus atoms. The triplet signal at −32.1 ppm is assignable to the *p*-tolylethynyl-substituted phosphorus atom, and the chemical shift is similar to that for the geminal isomer of $N_3P_3(C\equiv CPh)_2F_4$ (−23.2 ppm).[4] Therefore, the replacement of chloro groups in $(NPCl_2)_3$ by *p*-tolylethynyl groups results in the considerable upfield shift by 52.6 ppm of the ^{31}P signal in **1a**. Similarly, the $^{31}P\{^1H\}$ NMR spectrum of **1b** shows a doublet signal (−31.9 ppm) of the *p*-tolylethynyl-substituted phosphorus atoms and a triplet signal (18.9 ppm) of the chloro-substituted phosphorus atom. Since the $^{31}P\{^1H\}$ NMR spectrum of (phenylethynyl)pentafluorocyclotriphosphazene $N_3P_3(C\equiv CPh)F_5$ shows the signal of the phosphorus atom in the $P(C\equiv CPh)F$ moiety at 6.0 ppm,[4] similar chemical shifts are expected for those in $P\{C\equiv C(p\text{-Tol})\}Cl$ moieties of (*p*-tolylethynyl)chlorocyclotriphosphazenes, if any. However, in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture as well as those of **1a** and **1b**, there are no signals in the region between 15 and −25 ppm. This suggests that neither non-geminal isomers of **1a** and **1b** nor mono- or trisubstituted cyclotriphosphazenes were obtained as mentioned above. These NMR observations are consistent with the geminal configuration of **1a** and **1b**. The IR spectra of **1a** and **1b** exhibit a $C\equiv C$ stretching band at 2179 (**1a**) and 2177 (**1b**) cm^{-1}.

The crystal structure of **1a** was unequivocally determined by X-ray crystallography (Figure 1, Table 1). The N_3P_3 ring is puckered in a chair-type geometry: P1 and N2 deviate from the mean plane of P2, P3, N1, and N3 by 0.37 and −0.28 Å, respectively. The P–N bonds for the *p*-tolylethynyl-substituted phosphorus atom P1 [P1–N1: 1.6128(17) Å, P1–N3: 1.6088(17) Å] are longer than the other P–N bonds for the chloro-substituted phosphorus atoms P2 and P3 [1.5644(17)–1.5877(17) Å] that are close to those in $(NPCl_2)_3$ [av. 1.581(3) Å].[17] This elongation is attributable to the electron donation of the alkynyl

groups to the phosphorus atom P1 as also observed in several mono- and diorgano-substituted cyclotriphosphazenes.[18,19] The N1–P1–N3 angle [115.13(9)°] is narrower than the other N–P–N angles [av. 119.17(9)°]. Similar reduction of the corresponding N–P–N angles was observed in geminally substituted dialkyl- or diarylcyclotriphosphazenes $N_3P_3R_2Cl_4$ (R = alkyl, aryl).[19] We could not get single crystals of **1b** suitable for a full X-ray structure analysis, but a tentative analysis using a low-quality crystal of **1b** revealed a N_3P_3 ring structure containing four *p*-tolylethynyl and two chloro groups bonded geminally to phosphorus atoms.
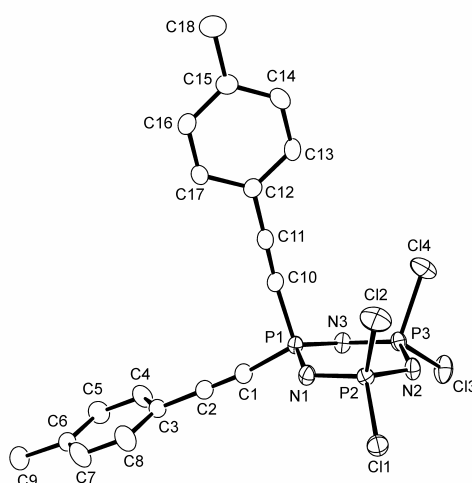
Figure 1. Crystal structure of **1a**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

**Table 1.** Selected bond distances (Å) and angles (°) in **1a**.

P1–N1	1.6128(17)	P1–N3	1.6088(17)	P2–N1	1.5644(17)
P2–N2	1.5857(17)	P3–N2	1.5877(17)	P3–N3	1.5735(17)
P1–C1	1.731(2)	P1–C10	1.741(2)	P2–Cl1	1.9823(8)
P2–Cl2	2.0193(8)	P3–Cl3	1.9792(8)	P3–Cl4	2.0179(9)
C1–C2	1.196(3)	C10–C11	1.202(3)		
N1–P1–N3	115.13(9)	N1–P2–N2	119.10(9)	N2–P3–N3	119.24(9)
P1–N1–P2	119.62(10)	P2–N2–P3	117.65(10)	P1–N3–P3	118.03(10)
C1–P1–C10	105.35(10)	Cl1–P2–Cl2	100.76(3)	Cl3–P3–Cl4	101.16(3)
P1–C1–C2	170.39(19)	P1–C10–C11	167.83(19)		

To prepare more highly substituted cyclotriphosphazenes with *p*-tolylethynyl groups, the reaction of $(NPCl_2)_3$ with ca. 6 equiv of LiC≡C(*p*-Tol) was investigated. But, the reaction resulted in a complicated mixture. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows only one sharp singlet signal at –31.3 ppm with weak intensity accompanied by unresolved broad signals in the region between –40 and 30 ppm. The chemical shift of the singlet signal is comparable to those for the *p*-tolylethynyl-substituted

phosphorus atoms in **1a** and **1b**, and thus the signal would be assignable to hexakis(*p*-tolylethynyl)cyclotriphosphazene $N_3P_3\{C\equiv C(p\text{-Tol})\}_6$ (**1c**). However, the content of **1c** in the mixture is considerably low, and the isolation of the pure form of **1c** has been unsuccessful (see Experimental section). Undesired reactions, e.g., ring cleavage of cyclotriphosphazene,[2,12] may have predominantly occurred to form unidentified products.

Reactions of the ligand precursors 1a and 1b with Co₂(CO)₈

To estimate the ability of (*p*-tolylethynyl)cyclotriphosphazenes **1a** and **1b** as multidentate ligands, we investigated the reactions of **1a** and **1b** with octacarbonyldicobalt, which is well known to react with an alkyne molecule to give a Co_2C_2 cluster. Thus, the reaction of **1a** with 2 equiv of $Co_2(CO)_8$ in toluene at room temperature produced a tetranuclear cobalt cluster $N_3P_3\{C_2Co_2(CO)_6(p\text{-Tol})\}_2Cl_4$ (**2**) in 94% yield (eq. 2). The structure of **2** was elucidated by spectroscopy (NMR, IR, and MS), elemental analysis, and X-ray crystallography (vide infra). The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two inequivalent signals: one doublet at 17.0 ppm assigned to the chloro-substituted phosphorus atoms and one triplet at 26.6 ppm assigned to the *p*-tolylethynyl-substituted phosphorus atom. The chemical shift of the latter signal is similar to that for the alkynyl-substituted phosphorus atom in the geminal isomer of tetranuclear cobalt cluster $N_3P_3\{C_2Co_2(CO)_6(Ph)\}_2F_4$ (32.5 ppm).[8] In comparison of the ^{31}P resonances of **2** with those of **1a**, the former signal of PCl₂'s is slightly (2.3 ppm) upfield shifted, while the latter signal is significantly downfield shifted by 58.7 ppm due to the coordination of the alkynyl substituents to cobalt. The coupling constant between the inequivalent phosphorus atoms ($^2J_{PP}$ = 8.1 Hz) is considerably decreased compared to **1a** ($^2J_{PP}$ = 45 Hz). Similar decrease of the P–P coupling constant has also been observed by conversion of $N_3P_3(C\equiv CPh)_2F_4$ ($^2J_{PP}$ = 91.1 Hz) to cluster $N_3P_3\{C_2Co_2(CO)_6(Ph)\}_2F_4$ ($^2J_{PP}$ = 50.1 Hz).[4,8] In the IR spectrum of **2**, the C≡C stretching band observed in **1a** (2179 cm^{-1}) disappeared and a new band assignable to the C–C stretching of Co_2C_2 cluster units appeared at 1576 cm^{-1}.
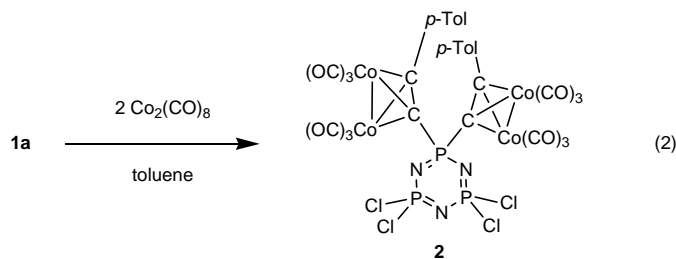
The X-ray structure analysis of the tetranuclear cobalt cluster **2** confirmed the molecular structure consisting of a N_3P_3 6-membered ring and two Co_2C_2 tetrahedral cluster units (Figure 2, Table 2). This is the first detailed report on the crystal structure analysis of bis(hexacarbonyldicobalt) complexes of dialkynylcyclotriphosphazenes. The N_3P_3 ring is slightly puckered: P2 and N2 deviate from the

least-squares plane of P1, P3, N1, and N3 by 0.16 and 0.27 Å, respectively. The N_3P_3-ring distortion seen in the P–N bonds and N–P–N angles are similar to that in **1a**. Thus, the P1–N1 and P1–N3 bonds [av. 1.616(2) Å] are longer than the other P–N bonds [av. 1.573(2) Å], and the N1–P1–N3 angle [115.16(9)°] is narrower than the other N–P–N angles [av. 119.6(1)°]. The considerable decrease of the s-character in the alkynyl C≡C bonds in **2** compared to the corresponding free ligand **1a** leads to the geometric changes in the P–C≡C moieties as follows: longer P1–C bond distances in **2** [av. 1.776(2) Å] compared to those in **1a** [av. 1.736(2) Å], narrower P1–C1–C2 and P1–C16–C17 angles in **2** [av. 144.4(2)°] compared to the corresponding P–C–C angles in **1a** [av. 169.1(2)°], and elongation of the alkynyl C–C bonds by ca. 0.15 Å from **1a** to **2**. The wider C1–P1–C16 angle [109.18(10)°] compared to the corresponding angle in **1a** [C1–P1–C10: 105.35(10)°] reflects the larger steric repulsion between the Co_2C_2 units in **2**.
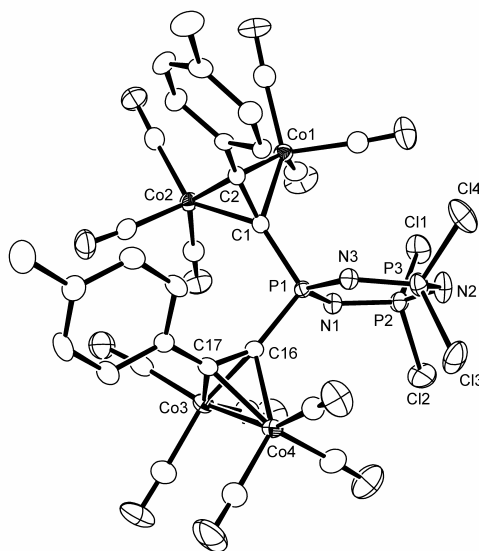

Figure 2. Crystal structure of **2**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) in **2**.

Co1–Co2	2.4590(7)	Co3–Co4	2.4672(7)	Co1–C1	1.992(2)
Co1–C2	1.985(2)	Co2–C1	1.962(2)	Co2–C2	1.964(2)
Co3–C16	1.961(2)	Co3–C17	1.969(2)	Co4–C16	1.982(2)
Co4–C17	1.971(2)	C1–C2	1.346(3)	C16–C17	1.347(3)
P1–N1	1.6129(18)	P1–N3	1.6184(18)	P2–N1	1.5648(18)
P2–N2	1.582(2)	P3–N2	1.579(2)	P3–N3	1.5678(18)
P1–C1	1.773(2)	P1–C16	1.779(2)	P2–Cl1	1.9999(10)
P2–Cl2	2.0032(10)	P3–Cl3	2.0146(10)	P3–Cl4	1.9925(11)
N1–P1–N3	115.16(9)	N1–P2–N2	119.60(10)	N2–P3–N3	119.51(10)
P1–N1–P2	122.57(11)	P2–N2–P3	119.29(12)	P1–N3–P3	121.92(11)
C1–P1–C16	109.18(10)	Cl1–P2–Cl2	100.37(4)	Cl3–P3–Cl4	99.87(4)
P1–C1–C2	145.55(18)	P1–C16–C17	143.30(17)		

The reaction of **1b** with excess $Co_2(CO)_8$ (ca. 5 equiv) in C_6D_6 at room temperature in a sealed NMR tube was monitored by ^{1}H NMR spectroscopy. The spectroscopic analysis of the final reaction mixture indicates the formation of hexanuclear cluster having an unreacted *p*-tolylethynyl group $N_3P_3\{C_2Co_2(CO)_6(p\text{-Tol})\}_3\{C{\equiv}C(p\text{-Tol})\}Cl_2$ (**3**) as a major product in 88% NMR yield (eq. 3).[20] No signals assignable to octanuclear cluster $N_3P_3\{C_2Co_2(CO)_6(p\text{-Tol})\}_4Cl_2$, in which all the four alkynyl groups are coordinated to cobalt atoms, have observed. The incomplete reaction is probably due to the steric hindrance in cluster **3** that prevents further complexation of a $Co_2(CO)_6$ fragment with the remaining *p*-tolylethynyl group. The ^{1}H NMR spectrum of product **3** shows four inequivalent methyl signals of the *p*-tolylethynyl groups with 1 : 1 : 1 : 1 intensity ratio. The $^{31}P\{^{1}H\}$ NMR spectrum of **3** exhibits three inequivalent signals of the phosphrous atoms in the N_3P_3 ring at 1.1, 17.7, and 24.1 ppm. Comparing the ^{31}P NMR chemical shifts of **3** with those in **2** (PCl_2: 17.0 ppm, $P\{C_2Co_2(CO)_6(p\text{-Tol})\}_2$: 26.6 ppm), the signals at 17.7 and 24.1 ppm can be assigned to the phosphorus atoms in the PCl_2 and $P\{C_2Co_2(CO)_6(p\text{-Tol})\}_2$ moieties, respectively. The third signal at 1.1 ppm is assignable to the phosphorus atom in the partially complexed $P\{C_2Co_2(CO)_6(p\text{-Tol})\}\{C{\equiv}C(p\text{-Tol})\}$ moiety, which is downfield shifted by 33 ppm compared to the signal (−31.9 ppm) of the *p*-tolylethynyl-substituted phosphorus atoms in **1b**. The analogous 32 ppm downfield-shift by coordination of one alkynyl group on cyclotriphosphazene to a $Co_2(CO)_6$ fragment has been reported for the reaction of (phenylethynyl)pentafluorocyclotriphosphazene $N_3P_3(C{\equiv}CPh)F_5$ with $Co_2(CO)_8$ to give $N_3P_3\{C_2Co_2(CO)_6(Ph)\}F_5$.[8] In the high-resolution electrospray mass spectrometry of the reaction mixture, the peak (m/z = 1545.5847) assignable to the Na^+ adduct of the parent molecule was observed when NaI was added to the sample. The IR spectrum of the reaction mixture shows four terminal CO stretching bands of **3** in the range of $2033-2100$ cm^{-1}. These observations support the structural characterization of **3**. Since the C_6D_6 or toluene solution of product **3** is thermally unstable under nitrogen atmosphere at room temperature, we have not succeeded in isolation of **3** from the reaction mixture in a synthetic-scale experiment. This makes the further characterization of **3** difficult. The thermal lability would be caused by the facile dissociation of CO ligands in **3**. This was supported by the experimental result that the decomposition of **3** in toluene solution was accelerated under reduced pressure.
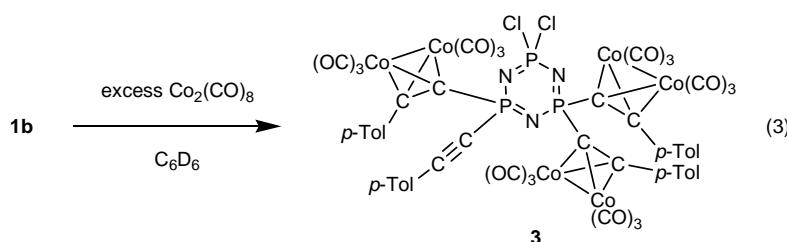
CONCLUSION

We synthesized (*p*-tolylethynyl)chlorocyclotriphosphazenes **1a** and **1b** by the salt elimination reaction between $(NPCl_2)_3$ and $LiC{\equiv}C(p\text{-Tol})$. The products were isolated in pure form and characterized. The capability of **1a** and **1b** as multidentate ligands was confirmed by their reactions with $Co_2(CO)_8$, where tetra- and hexanuclear cobalt clusters **2** and **3** were obtained from **1a** and **1b**, respectively. It is worth noting that **1b** is the first example of the cyclotriphosphazene having four alkynyl groups and, of course, the hexanuclear structure of the cobalt cluster **3** is unprecedented. Our ongoing works are (1) exploration of a high-yield synthesis of hexaalkynylcyclotriphosphazene **1c**, (2) isolation and full-characterization of hexanuclear cobalt cluster **3**, and (3) investigation of the reactions of *p*-tolylethynyl-substituted phosphazenes **1a** and **1b** with other transition-metal complexes that provide different multinuclear clusters.

EXPERIMENTAL

General Procedures

All manipulations of air- and moisture-sensitive compounds were carried out under an inert atmosphere in a N_2-filled glovebox or using standard high-vacuum-line and Schlenk techniques. $CDCl_3$ was dried and vacuum-transferred from CaH_2, and then stored under nitrogen over 4 Å molecular sieves. Hexane and toluene were dried over sodium/benzophenone and distilled before use. Dehydrated THF was purchased from Kanto Chemical Co., Inc. and used without further purification. Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was recystallized with hot hexane. 4-Ethynyltoluene (Kanto Chemical) was dried over CaH_2 and distilled prior to use. Octacarbonyldicobalt $Co_2(CO)_8$ (Kanto Chemical) was purchased and used as received. Flash chromatography[14] was performed using silica gel 60N (Kanto Chemical, 40-50 μm, spherical, neutral) or activated alumina (Wako Pure Chemicals Industries, Ltd., 45 μm). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-300 Fourier transform spectrometer, and chemical shifts were reported in parts per million. The residual proton (C_6D_5H: 7.15 ppm, $CHCl_3$: 7.24 ppm) and the carbon (C_6D_6: 128.0 ppm, $CDCl_3$: 77.0 ppm) resonances of deuterated solvents were used as internal references for ^1H and ^{13}C resonances, respectively. Aromatic carbon or proton is abbreviated to ArC or ArH. $^{31}P\{^1H\}$ NMR chemical shifts were referenced to 85% H_3PO_4 as an external standard. Infrared spectra were recorded using a HORIBA FT-730 spectrometer. High-resolution mass spectra (HRMS) were collected on a Bruker Daltonics APEX-(III) spectrometer operating in the electrospray ionization (ESI) mode, when NaI was added to the sample. Elemental analyses were carried out using a Yanaco MT-6 and a Yanaco HNS-15/HSU-20 microanalyzers. Mass spectrometric analyses and elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

Synthesis of N$_3$P$_3$\{C≡C(p-Tol)\}$_2$Cl$_4$ (1a) and N$_3$P$_3$\{C≡C(p-Tol)\}$_4$Cl$_2$ (1b)

A THF/hexane solution of p-tolylethynyllithium LiC≡C(p-Tol) was prepared as follows: To a solution of 4-ethynyltoluene (1.165 g, 10.03 mmol) in THF (30 mL) was slowly added n-BuLi (1.52 M in hexane, 7.5 mL, 11 mmol) via a syringe at ca. −90 °C, and then the mixture was stirred for 1 h at this temperature. To this solution of LiC≡C(p-Tol) was added dropwise a solution of (NPCl$_2$)$_3$ (1.742 g, 5.011 mmol) in THF (40 mL) at −80 °C for 15 min. The yellow reaction mixture was allowed to warm up to room temperature. The reaction was monitored by ^{31}P\{^{1}H\} NMR spectroscopy until the relative intensity of signals became constant. After stirring at room temperature overnight, the dark-brown solution was evaporated under vacuum. The dark-brown residue was extracted three times with toluene (25, 7.5, 7.5 mL), and the extracts were centrifuged. The supernatants were combined and evaporated. The residue was separated by flash chromatography on silica gel (eluent: toluene/hexane 1 : 1), and three fractions were obtained. Evaporation of the first colorless fraction gave a colorless solid, and then recrystallization of the solid from toluene gave colorless crystals of **1a** in 54% yield (1.37 g, 2.71 mmol). From the second yellow fraction, an unidentified yellow oil (0.047 g) was obtained. From the third fraction, pale-yellow crystals of **1b** (0.180 g, 0.270 mmol) were obtained in 5% yield. The fourth fraction was obtained by elution with THF and was evaporated to give unidentified products as a brown oil (0.765 g).

Data for **1a**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.37 (s, 3H, CH$_3$), 7.18 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.49 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH). ^{31}P\{^{1}H\} NMR (121.5 MHz, CDCl$_3$): δ −32.1 (t, $^2J_{PP}$ = 45 Hz, P\{C≡C(p-Tol)\}$_2$), 19.3 (d, $^2J_{PP}$ = 45 Hz, PCl$_2$). ^{13}C\{^{1}H\} NMR (75.5 MHz, CDCl$_3$): δ 22.2 (s, CH$_3$), 83.0 (dt, $^1J_{CP}$ = 279 Hz, $^3J_{CP}$ = 7.6 Hz, C≡C(p-Tol)), 102.8 (dt, $^2J_{CP}$ = 54 Hz, $^4J_{CP}$ ~ 2 Hz, C≡C(p-Tol)), 116.4 (d, $^3J_{CP}$ = 5.3 Hz, ArC-ipso), 129.7 (s, ArC-meta), 133.1 (d, $^4J_{CP}$ = 2.0 Hz, ArC-ortho), 142.3 (s, ArC-para). IR (KBr-pellet): 2179 (s, $\nu_{C≡C}$), 1604 (w), 1508 (w), 1228 (s, ν_{NP}), 1196 (s, ν_{NP}), 874 (m), 816 (w), 611 (m), 565 (m), 519 (m), 463 (m), 424 (m) cm^{-1}. HRMS (ESI): m/z calcd for C$_{18}$H$_{14}$Cl$_4$N$_3$P$_3$Na: 527.9047, found: 527.9046 [M+Na]$^+$. Anal. Calcd (%) for C$_{18}$H$_{14}$Cl$_4$N$_3$P$_3$: C, 42.63; H, 2.78; N, 8.29; Cl, 27.97. Found: C, 42.59; H, 2.97; N, 8.18; Cl, 27.66.

Data for **1b**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.35 (s, 3H, CH$_3$), 7.11 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.45 (d, 2H, $^3J_{HH}$ = 8.0 Hz, ArH). ^{31}P\{^{1}H\} NMR (121.5 MHz, CDCl$_3$): δ −31.9 (d, $^2J_{PP}$ = 41 Hz, P\{C≡C(p-Tol)\}$_2$), 18.9 (t, $^2J_{PP}$ = 41 Hz, PCl$_2$). ^{13}C\{^{1}H\} NMR (75.5 MHz, CDCl$_3$): δ 21.7 (s, CH$_3$), 84.4 (ddd, $^1J_{CP}$ = 275 Hz, $^3J_{CP}$ = 7.8, 0.9 Hz, C≡C(p-Tol)), 99.9–101.3 (m, C≡C(p-Tol)), 116.8 (virtual t, J_{CP} = 2.6 Hz, ArC-ipso), 129.2 (s, ArC-meta), 132.7 (s, ArC-ortho), 141.2 (s, ArC-para). IR (KBr-pellet): 2177 (s, $\nu_{C≡C}$), 1604 (w), 1508 (w), 1190 (s, ν_{NP}), 1174 (s, ν_{NP}), 868 (m), 839 (w), 814 (m), 781 (w), 768 (w), 611 (m), 573 (m), 563 (m), 546 (m), 538 (m), 474 (m), 459 (m) cm^{-1}. HRMS (ESI): m/z calcd for C$_{36}$H$_{28}$Cl$_2$N$_3$P$_3$Na: 688.0765, found: 688.0768 [M+Na]$^+$. Anal. Calcd (%) for C$_{36}$H$_{28}$Cl$_2$N$_3$P$_3$: C, 64.88; H, 4.23; N, 6.31; Cl,

10.63. Found: C, 64.53; H, 4.53; N, 6.22; Cl, 10.38.

The reaction of $(NPCl_2)_3$ with ca. 6 equiv of $LiC\equiv C(p\text{-}Tol)$

A solution of p-tolylethynyllithium $LiC\equiv C(p\text{-}Tol)$ was prepared by slow addition of n-BuLi (1.57 M in hexane, 14 mL, 22 mmol) to a solution of 4-ethynyltoluene (2.36 g, 20.3 mmol) in THF (18 mL) at 0 °C followed by stirring of the mixture for 1 h. The mixture was allowed to warm to room temperature, and a solution of $(NPCl_2)_3$ (1.16 g, 3.34 mmol) in THF (5 mL) was added dropwise to the mixture over 30 min. After stirring for 3.5 h at room temperature, the reaction was quenched by adding methanol (3.5 mL) at 0 °C. Evaporation of volatiles under vacuum gave a dark-brown oil (5.79 g). The residual oil was extracted with toluene (65 mL), and the extract was centrifuged. After the supernatant was concentrated under vacuum, the dark-brown residue (2.96 g) was separated by flash chromatography on alumina (eluent: THF/toluene 1 : 300). Evaporation of the second fraction gave a yellow oil, and then trituration and washing of the solid with hexane yielded a yellow powder containing hexakis(p-tolylethynyl)cyclotriphosphazene $N_3P_3\{C\equiv C(p\text{-}Tol)\}_6$ (**1c**) as a major component (0.020 g). Attempt to isolate pure **1c** from the yellow powder was unsuccessful.

Data assignable to **1c** in the yellow powder: ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.33 (s, 3 H, CH$_3$), 7.06 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, ArH), 7.42 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, ArH). ^{31}P$\{^1$H$\}$ NMR (121.5 MHz, CDCl$_3$): δ −31.3 (s, P$\{C\equiv C(p\text{-}Tol)\}_2$).

Synthesis of $N_3P_3\{C_2Co_2(CO)_6(p\text{-}Tol)\}_2Cl_4$ (2)

A solution of **1a** (0.469 g, 0.925 mmol) in toluene (12 mL) was added to a solution of Co$_2$(CO)$_8$ (0.704 g, 2.06 mmol) in toluene (12 mL) with stirring. After stirring the mixture for 40 min at room temperature, volatiles were removed under vacuum. The dark-red residue was dissolved in a mixture of CH$_2$Cl$_2$ (8 mL) and hexane (4 mL). Cooling of the solution at −30 °C afforded dark-red crystals as the first crop (0.747 g, 0.692 mmol). Concentration and cooling of the mother liquor at −30 °C gave the second crop (0.194 g, 0.180 mmol). Total yield: 94%.

Data for **2**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.31 (s, 3 H, CH$_3$), 7.00 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.48 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, ArH). ^{31}P$\{^1$H$\}$ NMR (121.5 MHz, CDCl$_3$): δ 17.0 (d, $^2J_{PP}$ = 8.1 Hz, PCl$_2$), 26.6 (t, $^2J_{PP}$ = 8.1 Hz, P$\{C_2Co_2(CO)_6(p\text{-}Tol)\}_2$). ^{13}C$\{^1H\}$ NMR (75.5 MHz, CDCl$_3$): δ 21.5 (s, Me), 76.8 (dt, $^1J_{CP}$ = 149 Hz, $^3J_{CP}$ ~ 4 Hz, C−C(p-Tol)), 100.6 (s, C−C(p-Tol)), 129.6 (s, ArC), 130.1 (s, ArC), 133.4 (s, ArC), 138.9 (s, ArC), 197.8 (br s, C≡O). IR (KBr-pellet): 2102 (m, ν_{CO}), 2094 (m, ν_{CO}), 2063 (s, ν_{CO}), 2044 (s, ν_{CO}), 2027 (s, ν_{CO}), 2015 (s, ν_{CO}), 2008 (m, ν_{CO}), 1576 (w, ν_{C-C}), 1491 (w), 1209 (m, ν_{NP}), 1186 (m, ν_{NP}), 582 (m), 569 (w), 511 (m), 492 (w) cm^{-1}. HRMS (ESI): m/z calcd for C$_{30}$H$_{14}$O$_{12}$Cl$_4$N$_3$P$_3$Co$_4$Na: 1099.5765, found: 1099.5759 [M+Na]$^+$. Anal. Calcd (%) for C$_{30}$H$_{14}$O$_{12}$Cl$_4$N$_3$P$_3$Co$_4$: C, 33.40; H, 1.38; N, 3.89; Cl, 13.14. Found: C, 32.99; H, 1.38; N, 3.80; Cl, 12.89.

Monitoring the reaction of 1b with excess (ca. 5 equiv) $Co_2(CO)_8$

An NMR tube with a J. Young valve (5 mm o.d.) was charged with **1b** (5 mg, 8 μmol), $(C_5H_5)_2Fe$ (less than 1 mg) as an internal standard, and C_6D_6 (0.46 mL). After measuring a ^{1}H NMR spectrum of the solution to determine the intensity ratio of **1b** to $(C_5H_5)_2Fe$, the solution was transferred to a Pyrex NMR tube, and then the washing of the J. Young NMR tube with C_6D_6 (ca. 0.1 mL) was added. $Co_2(CO)_8$ (13 mg, 38 μmol) was then added to the Pyrex NMR tube, and the C_6D_6 (ca. 0.1 mL) washing of the beaker and funnel, which had been used for weighing and transferring $Co_2(CO)_8$, was also added. After the Pyrex NMR tube was flame-sealed under vacuum, the mixture was allowed to stand at room temperature for 22 h. During that time, the reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, showing the formation of $N_3P_3\{C_2Co_2(CO)_6(p\text{-}Tol)\}_3\{C{\equiv}C(p\text{-}Tol)\}Cl_2$ (**3**) in 88% NMR yield. Then the tube was opened, and the HRMS and IR spectrum of **3** in the C_6D_6 solution were measured.

Data for **3**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.86 (s, 3 H, CH_3), 1.96 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 6.77 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, ArH), 6.85 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, ArH), 6.95 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, ArH), 6.97 (d, 2 H, $^3J_{HH}$ = 8.6 Hz, ArH), 7.57 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, ArH), 7.85 (d, 2 H, $^3J_{HH}$ = 8.6 Hz, ArH), 7.88 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, ArH), 7.93 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 1.1 (dd, $^2J_{PP}$ = 6.1 Hz, $^2J_{PP}$ = 12.6 Hz, P$\{C_2Co_2(CO)_6(p\text{-}Tol)\}\{C{\equiv}C(p\text{-}Tol)\}$), 17.7 (t, $^2J_{PP}$ = 12.6 Hz, PCl_2), 24.1 (dd, $^2J_{PP}$ = 6.1 Hz, $^2J_{PP}$ = 12.6 Hz, P$\{C_2Co_2(CO)_6(p\text{-}Tol)\}_2$). IR ($C_6D_6$): 2100 (w, ν_{CO}), 2092 (w, ν_{CO}), 2069 (s, ν_{CO}), 2033 (s, ν_{CO}) cm^{-1}. HRMS (ESI): m/z calcd for $C_{54}H_{28}O_{18}Cl_2N_3P_3Co_6Na$: 1545.5842, found: 1545.5847 [M+Na]$^+$.

X-Ray crystal structure determination

X-Ray quality single crystals of **1a** were obtained by recrystallization from toluene as colorless blocks and those of **2** from CH_2Cl_2/hexane as dark-red blocks. Intensity data for the analysis were collected on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) under a cold nitrogen stream (T = 173 K). Numerical absorption corrections were applied to the data. The structures were solved by direct method using the SHELXS-97 program[21] for **1a** or the Patterson method using the DIRDIF-99 program[22] for **2** and refined by full matrix least-squares techniques on all F^2 data with SHELXL-97.[21] Anisotropic refinement was applied to all non-hydrogen atoms, and all the hydrogen atoms were put at calculated positions. CCDC-700217 (**1a**) and 700218 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for **1a**: $C_{18}H_{14}Cl_4N_3P_3$, M = 507.03, monoclinic, space group $P2_1/n$ (no. 14), a = 10.623(3) Å, b = 17.038(5) Å, c = 12.194(4) Å, β = 90.4320(13)°, V = 2207.0(12) Å^3, Z = 4, D_{calc} = 1.526 g cm^{-3}, μ(Mo−Kα) = 0.76 mm^{-1}, 15524 reflections measured, 4783 unique (R_{int} = 0.040), $R1$ = 0.044 and $wR2$ = 0.082 (all data).

Crystallographic data for **2**: $C_{30}H_{14}Cl_4Co_4N_3O_{12}P_3$, M = 1078.87, triclinic, space group P-1 (no. 2), a =

9.050(3) Å, b = 11.436(4) Å, c = 20.122(6) Å, α = 74.483(8)°, β = 79.287(9)°, γ = 88.179(10)°, V = 1971.4(11) Å^3, Z = 2, D_{calc} = 1.818 g cm^{-3}, μ(Mo–Kα) = 2.11 mm^{-1}, 14183 reflections measured, 8395 unique (R_{int} = 0.030), $R1$ = 0.036 and $wR2$ = 0.066 (all data).

ACKNOWLEDGEMENTS

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