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# Cyclodiphosphazanes as synthetic probes: P-C/P-N bond formation from the reaction with functionalized propargyl alcohols and *N*-hydroxy substrates

G GANGADHARARAO and K C KUMARA SWAMY*
School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
e-mail: kckssc@uohyd.ac.in; kckssc@yahoo.com

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**Abstract.** Phosphano-indoles were synthesized in a fairly straightforward route from the reaction of simple cyclodiphosphazanes [XP($\mu$-N-*t*-Bu)$_2$PY] [X = Y= NH-*t*-Bu (**1a**); X = Y = NH-*i*-Pr (**1b**)] with *o*-aminophenyl functionalized propargyl alcohols. The reaction occurs via an allene intermediate formed by $P^{III}$-O-C $\rightarrow$ $P^{V}$(O)-C rearrangement, followed by cyclization utilizing the central allenic carbon and the –$NH_2$ functionality. In a similar way, cyclodiphosphazanes [XP($\mu$-N-*t*-Bu)$_2$PY] [X = Y = Cl (**1c**); X = Cl, Y = NH-*t*-Bu (**1d**)] have been treated with *N*-hydroxy substrates to obtain novel $P^{III}$-O-N $\rightarrow$ $P^{V}$(O)-N rearranged products. X-ray structures of the four products, 2-(1-phenyl-ethyl)-3-[(*t*-Bu)NH)P($\mu$-N-*t*-Bu)$_2$P(O)]-indole [**14**], *cis*-{[-C(=O)-$C_6H_4$-C(=O)-]-N-P(=O)-N-*t*-Bu}$_2$ [*cis*-**18**], *trans*-{[-C(=O)-$C_6H_4$-C(=O)-]-N-P(=O)-N-*t*-Bu}$_2$ [*trans*-**18**] and *cis*-[(*t*-BuNH)P($\mu$-N-*t*−Bu)$_2$P(=O)-N{ -C(=O)-$CH_2$-$CH_2$-C(=O)-}] [*cis*-**19**] are also reported.

**Keywords.** Cyclodiphosphazanes; *cis–trans* isomerism; allenes; indoles; rearrangement; propargyl alcohols; phosphano-heterocycles.

## 1. Introduction

Cyclodiphosph(III)azanes and their derivatives are well-established inorganic ring systems with alternate phosphorus and nitrogen atoms in their four-membered cyclic skeleton.[1] Earlier, many studies in chemistry focused on the substitution reactions involved in the P-Cl bond and the relative geometry of the substituents on phosphorus.[1,2] Later, attention was shifted to utilize these ring systems as versatile ligands for metal complexes,[3] precursors for macrocycles[4] and synthetic probes to explore organic reaction pathways.[5] The nucleophilic reactivity of cyclodiphosph(III)azanes towards alkenes, alkynes, allenylphosphonates and azo compounds has been gainfully employed in isolating the species analogous to the proposed intermediates in the well-known Mitsunobu reaction as well as 'umpolung addition' via phosphine activation of alkynes.[5c,6] In the oxidative addition reactions, we have also reported rather unusual 'molecularly non-stoichiometric' crystals formed by this class of phosphorus compounds.[7] The steric protection offered by the two-ring N-*t*−Bu groups, convenient monitoring by $^{31}$P NMR, and good crystallinity of the products in most cases make these compounds wonderful precursors to probe organic reactions (chart 1).

In this study, although reaction of a normal alcohol or phenol with [ClP($\mu$-NR)]$_2$ leads to the substituted $P^{III}$ products, the reaction with propargyl alcohols affords tetracoordinate P-C bonded compounds *cis*-**10** and *trans*-**10** as shown in scheme 1a via a *pseudo*-Claisen-type rearrangement.[8] These are potentially polymerizable phosphorus-based systems with alkene/alkyne substituents at two ends that would ultimately lead to polymer-terminated phosphonic acids as the end products. Allenes, and their subclass allenylphosphonates (phosphorylated allenes), are versatile precursors for diverse applications in organic synthesis.[9–11] In this connection, recently, we reported the reactions of cyclodiphosphazanes with aryl substituted propargyl alcohols possessing *o*-nitro group that lead to rather previously unsuspected and unexpected products (e.g., **11**, **12**; scheme 1b).[12] As part of our continued interest in studying the reactivity of $P^{III}$ compounds, in this study, we describe the first systematic studies on the reactivity of cyclophosphazanes with (a) *o*-amino-functionalized propargyl alcohols that afford phosphorus-based indoles and (b) *N*-hydroxy substrates that lead to $P^{III}$-O-N $\rightarrow$ $P^{V}$(O)-N rearranged products. The latter study is in continuation of our recent study concerning

*For correspondence

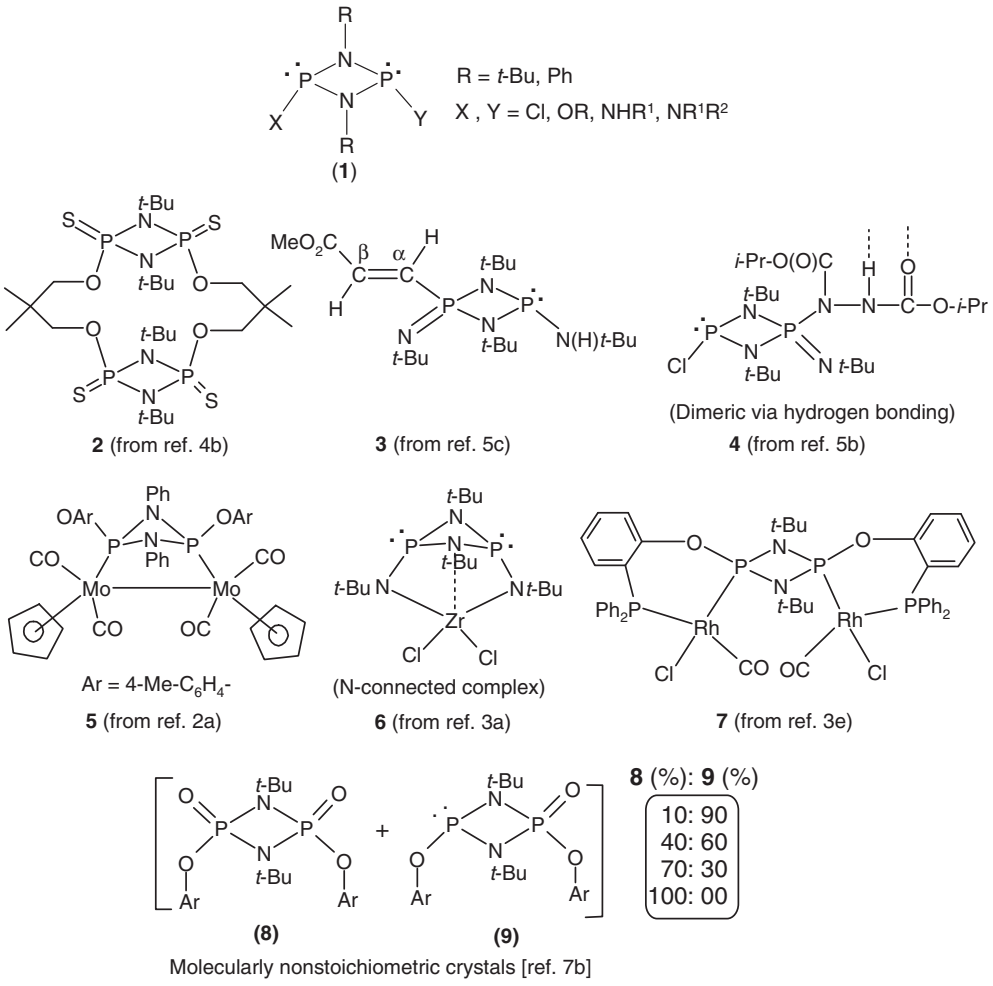



**Chart 1.** Compounds **2–9** showing the utility of cyclodiphosphazanes.

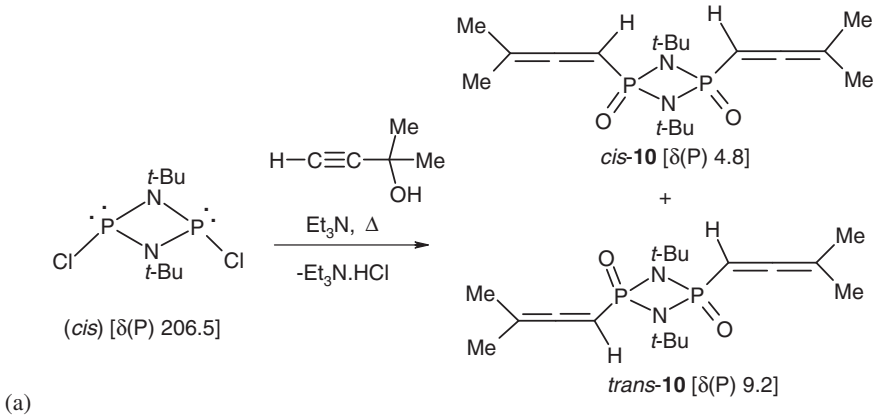
the reaction of cyclophosphazanes with *N*-hydroxy succinimide.[12,13]

## 2. Experimental

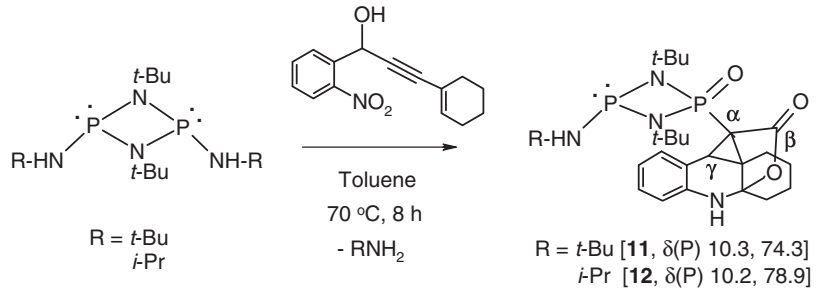
All synthesis and manipulations were performed under nitrogen atmosphere unless stated otherwise. Chemicals/solvents were purified as required using standard procedures,[14] unless otherwise noted. $^{1}$H, $^{13}$C, and $^{31}$P NMR spectra ($^{1}$H 400 MHz, $^{13}$C 100 MHz, and $^{31}$P 162 MHz) were recorded using a $CDCl_3$ solution (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% $H_3PO_4$ ($\delta = 0$). Melting points were determined by using a hot stage melting point apparatus and were uncorrected. For TLC, glass microslides were coated with silica-gel-$GF_{254}$ (mesh size 75 $\mu$) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100–200 mesh size was used. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using LC-MS and HRMS (ESI-TOF) equipment. Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer.

### 2.1 *Synthesis of functionalized propargyl alcohols (**13a–c**)-representative procedure for **13c***

A slightly modified literature procedure[15] was used here. To a round bottomed flask (50 mL) equipped with 2-iodoaniline (1.50 g, 6.80 mmol), $PdCl_2$ (0.03 g, 0.17 mmol), $PPh_3$ (0.09 g, 0.34 mmol), CuI (0.06 g, 0.34 mmol) and acetonitrile (20 mL), was added but-3-yn-2-ol (0.64 mL, 8.22 mmol) and $Et_3N$ (3.80 mL, 27.40 mmol) via syringe. Then, the mixture was stirred at room temperature (25°C) for 7 h and the progress of the reaction monitored by TLC. Upon completion of the reaction, the crude mixture was filtered, the solid residue was washed with EtOAc, and the combined organic extract was concentrated under reduced pressure. Purification by column chromatography (hexane: ethyl acetate 4:1) gave the desired 4-(2-aminophenyl)but-3-yn-2-ol (**13c**) as a gummy liquid.




(a)




(b)

**Scheme 1.** Reaction of PIII-Cl precursors with propargyl alcohols leading to allene **10** or polycycles **11**–**12**.

The known compounds **13a** and **13b**[15] were prepared by following the same procedure.

2.1a *Compound **13c***: Yield: 1.36 g (91%). $^1$H NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 7.27–6.66 (m, 4H, Ar-*H*), 4.78 (qrt, 1H, C*H*$CH_3$), 4.19 (br, 2H, N$H_2$), 3.41 (br, 1H, O*H*), 1.55 (d, $J$ = 6.4 Hz, 3H, CHC$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 147.8, 132.2, 129.7, 118.0, 114.5, 107.4 (Ar-*C*), 96.7 (*C* ≡C), 80.5 (C≡*C*), 58.7 (*C*H$(CH_3)_2$), 24.6 (CH*C*$H_3$). IR (KBr, cm$^{-1}$) 3359, 2980, 2931, 2219, 1616, 1490, 1457, 1364, 1314, 1161, 1101, 1079, 1029, 936, 744. LC-MS: *m*/*z* 162 [M+1]$^+$. Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.43; H, 6.75; N, 8.61.

## 2.2 *Synthesis of phosphazanyl indoles **14–17***

To a round bottomed flask (25 mL) equipped with cyclodiphosphazane [(*t*-BuNH)P($\mu$-N-*t*-Bu)]$_2$ (**1a**)[5c] (0.73 g, 2.1 mmol) and propargyl alcohol (**13a**)[15] (0.50 g, 2.1 mmol), was added dry toluene (8 mL). The mixture was stirred at 80°C for 4–5 h, cooled to room temperature upon which a white solid material settled down. This was then filtered and washed with diethyl ether (3 × 10 mL) to afford pure 2-(1-phenyl-ethyl),3-[(*t*-Bu)NH)P($\mu$-N-*t*-Bu)$_2$P(O)]-indole **14** as a white solid. Compounds **15–17** were prepared by following the same procedure.

2.2a *Compound **14***: Yield: 0.99 g (92%). mp: 252–256°C. $^1$H NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.28 (1 s, 1H, N*H*), 7.67–7.12 (m, 9H, Ar-*H*), 5.88 (qrt, 1H, C*H*-$CH_3$), 3.32 (d, $J$ = 7.6 Hz, 1H, N*H* − *t*-Bu), 1.74 (d, $J$ = 7.6 Hz, 3H, CH-C$H_3$), 1.38 (d, $J$ = 0.8 Hz, 9H, C(C$H_3$)$_3$), 1.26 and 1.14 (2 s, 18H, C(C$H_3$)$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 153.1 (d, $^2J$(P-C) ∼ 25.0 Hz, PC*C*-NH), 144.0, 135.7, 135.6, 129.1, 129.0, 128.6, 127.9, 126.5, 121.8, 120.6, 120.5, 120.4, 110.8, (Ar-*C*), 102.1 (d, $^1J$(P-C) ∼ 172.0 Hz, P-*C*), 52.6 (d, $^2J$(P-C) ∼ 5.0 Hz, *C*(CH$_3$)$_3$), 51.9 (d, $^2J$(P-C) ∼ 15.0 Hz, *C*(CH$_3$)$_3$), 35.9 (‘1 s, *C*H-CH$_3$), 32.9 (d, $^3J$(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 31.3 (d, $^3J$(P-C) = 5.0 Hz, C(*C*H$_3$)$_3$), 20.5 (1 s, CH-*C*H$_3$). $^{31}$P NMR (160 MHz, $CDCl_3$, ppm) $\delta$ 77.97 (d, $^2J$(P-P) = 10.0 Hz, (*P*-NH*t*-Bu), 10.67 (d, $^2J$(P-P) = 10.0 Hz, *P*-C). IR (KBr, cm$^{-1}$) 3353, 3162, 3123, 3079, 2964, 2866, 1425, 1364, 1194, 1123, 1074, 888, 838. HRMS (ESI) calcd. for $C_{28}H_{42}N_4OP_2$ (M + H)$^+$ 513.2913, found 513.2912.

2.2b *Compound **15***: This was prepared as a white solid by using [(*i*-PrNH)P($\mu$-N-*t*-Bu]$_2$ (**1b**)[5d]

(0.42 g, 1.31 mmol) and propargyl alcohol **13a** (0.31 g, 1.31 mmol) Yield: 0.529 g (81%). mp: 264–268°C. $^1$H NMR (400 MHz, $CDCl_3$, ppm) $\delta$ 8.50 (1 s, 1H, N*H*), 7.66–7.12 (m, 9H, Ar-*H*), 5.91 (qrt, 1H, C*H*-$CH_3$), 3.65 (br, 1H, NH-C*H*$(CH_3)_2$), 3.01 (br, 1H, N*H* − *i*-Pr), 1.75 (d, $J$ = 7.2 Hz, 3H, CH-C*H*$_3$), 1.24–1.22 (m, 6H, NH-CH(C*H*$_3)_2$), 1.25 and 1.14 (2 s, 18H, C(C*H*$_3)_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) $\delta$ 153.4 (d, $^2J$(P-C) ∼ 25.0 Hz, PC*C*-NH), 144.1, 135.9, 135.7, 129.1, 128.9, 128.5, 128.3, 127.9, 126.4, 121.7, 120.6, 120.5, 120.3, 110.9 (Ar-*C*), 101.6 (d, $^1J$(P-C) ∼ 172.0 Hz, P-*C*), 52.5 (*C*$(CH_3)_3$), 44.9 (1 s, NH-*C*H$(CH_3)_2$), 35.9 (1 s, *C*H-$CH_3$), 31.2 (1 s, C(*C*H$_3)_3$), 26.5 (1 s, NH-CH(*C*H$_3)_2$), 20.6 (1 s, CH-*C*H$_3$). $^{31}$P NMR (160 MHz, $CDCl_3$, ppm) $\delta$ 82.67 (br, *P*-NH-*i*-Pr), 10.48 (br, 1P, *P*-C). IR (KBr, cm$^{-1}$) 3381, 3167, 3123, 3090, 3024, 2968, 2926, 2871, 1528, 1456, 1433, 1391, 1363, 1293, 1197, 1133, 1070, 891, 802. HRMS (ESI) calcd for $C_{27}H_{40}N_4OP_2$ $(M + H)^+$ 499.2756, found 499.2757.

2.2c *Compound **16***: This was prepared as a white solid by using **1a** (0.64 g, 1.83 mmol) and propargyl alcohol **13b** (0.32 g, 1.83 mmol) Yield: 0.74 g (90%). mp: 296–298°C. $^1$H NMR (400 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 7.78 (br, 1H, N*H*), 7.60-7.10 (m, 4H, Ar-*H*), 4.37 (m, 1H, C*H*$(CH_3)_2$, 3.51 (br, 1H, N*H* − *t*-Bu), 1.40 (1 s, 9H, C(C*H*$_3)_3$), 1.35, (1 s, 6H, CH(C*H*$_3)_2$), 1.19 (1 s, 18H, C(C*H*$_3)_3$). $^{13}$C NMR (100 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 155.7 (d, $^2J$(P-C) ∼ 27.0 Hz, PC*C*-NH), 135.8, 128.3, 120.9, 119.5, 119.4, 110.3 (Ar-*C*), 98.0 (d, $^1J$(P-C) ∼ 176.0 Hz, P-*C*), 52.0 (d, $^2J$(P-C) ∼ 6.0 Hz, *C*$(CH_3)_3$), 51.0 (d, $^2J$(P-C) ∼ 14.0 Hz, *C*$(CH_3)_3$), 32.0 (d, $^3J$(P-C) = 10.0 Hz, C(*C*H$_3)_3$), 30.4 (1 s C(*C*H$_3)_3$), 26.8 (1 s, *C*H$(CH_3)_2$, 25.0 and 21.3 (2 s, CH(*C*H$_3)_2$). $^{31}$P NMR (162 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 78.52 (d, $^2J$(P-P) = 9.5 Hz, (*P*-NH*t*-Bu), 13.48 (d, $^2J$(P-P) = 9.5 Hz, *P*-C). IR (KBr, cm$^{-1}$) 3359, 3140, 2970, 2860, 1485, 1458, 1430, 1359, 1288, 1211, 1129, 1058, 1030, 992, 878. HRMS (ESI) calcd. for $C_{23}H_{40}N_4OP_2$ $(M + Na)^+$ 473.2575, found 473.2577.

2.2d *Compound **17***: This was prepared as a white solid by using **1a** (0.32 g, 0.91 mmol) and propargyl alcohol **13c** (0.15 g, 0.91 mmol) Yield: 0.35 g (88%). mp: 278–280°C. $^1$H NMR (400 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 7.75 (1 s, 1H, N*H*), 7.60–7.07 (m, 4H, Ar-*H*), 4.09 (d, $J$ = 7.6 Hz, 1H, N*H* − *t*−Bu), 3.22 (qrt, 2H, C*H*$_2$CH$_3$), 1.40 (1 s, 9H, C(C*H*$_3)_3$), 1.35 (t, 3H, CH$_2$C*H*$_3$), 1.19 (1 s, 18H, C(C*H*$_3)_3$). $^{13}$C NMR (100 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 151.5 (d, $^2J$(P-C) ∼ 25.0 Hz, PC*C*-NH), 135.5, 128.5, 128.3, 120.7, 119.2, 119.0, 110.0 (Ar-*C*), 98.4 (d, $^1J$(P-C) ∼ 177.0 Hz, P-*C*), 51.8 (d, $^2J$(P-C) ∼ 7.0 Hz, *C*$(CH_3)_3$), 50.8 (d, $^2J$(P-C) ∼ 15.0 Hz, *C*$(CH_3)_3$), 31.6 (d, $^3J$(P-C) = 10.0 Hz, C(*C*H$_3)_3$), 30.0 (d, $^3J$(P-C) = 5.0 Hz, C(*C*H$_3)_3$), 19.7 (1 s, *C*H$_2$CH$_3$), 12.7 (1 s, CH$_2$*C*H$_3$). $^{31}$P NMR (162 MHz, $CDCl_3$+$CD_3OD$, ppm) $\delta$ 82.6 (d, $^2J$(P-P) = 9.2 Hz, (*P*-NH*t*-Bu), 17.5 (d, $^2J$(P-P) = 9.2 Hz, *P*-C). IR (KBr, cm$^{-1}$) 3359, 3090, 2964, 1458, 1436, 1364, 1288, 1195, 1129, 1063, 992, 888. HRMS (ESI) calcd for $C_{22}H_{38}N_4OP_2$ $(M + H)^+$ 437.2600, found 437.2601.

2.3 *Synthesis of cis- and trans-{[-C(= O) − $C_6H_4$− C(=O)-]-N-P(=O)-N-t-Bu}$_2$ (cis-**18** and trans-1 **8**)*

To a solution of *N*-hydroxy phthalimide (0.494 g, 3.02 mmol) and $NEt_3$ (0.46 ml, 3.33 mmol) in THF (20 mL) was added [ClP-N(*t*-Bu)]$_2$ (**1c**)[16] (0.417 g, 1.51 mmol) dissolved in THF (10 mL) drop-wise at 0°C over a period of 15 min. Then, the contents were brought to room temperature and stirred for 24 h. After removal of amine hydrochloride (filtration) and solvent, the crude product was purified by column chromatography (hexane/EtOAc; 3:2) to afford *cis*-**18** (white solid) followed by *trans*-**18** (white solid). *Cis*-**18** was crystallized from ethyl acetate and *trans*-**18** was crystallized from dichloromethane.

2.3a *Cis-**18***: Yield 0.115 g (14%); mp 248–250°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90–7.88 (m, 4H), 7.84–7.82 (m, 4H), 1.52 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.6, 135.3, 132.2, 124.3, 58.0, 30.1. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ −17.40. IR (KBr, cm$^{-1}$) 3090, 3047, 2970, 2871, 1781, 1737, 1600, 1468, 1364, 1293, 1255, 1167, 1085, 1003, 904, 866. HRMS (ESI) calcd for $C_{24}H_{26}N_4O_6P_2$ $(M + H)^+$ 529.1407, found: 529.1407.

2.3b *Trans-**18***: Yield 0.651 g (82%); mp 250–252°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04–8.02 (m, 4H), 7.88–7.86 (m, 4H), 1.39 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.2, 135.5, 132.3, 124.7, 56.8, 30.0. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ −20.36. IR (KBr, cm$^{-1}$) 3083, 2976, 2928, 1794, 1748, 1717, 1645, 1599, 1468, 1373, 1300, 1265, 1192, 1148, 1051, 1015, 916. HRMS (ESI) calcd. for $C_{24}H_{26}N_4O_6P_2$ $(M + H)^+$ 529.1407, found: 529.1406.

2.4 *Synthesis of cis- and trans- [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)-N{-C(=O)-CH$_2$-CH$_2$ − C(=O)-}] (cis-**19** and trans-**19**)*

The procedure was similar to that for compound **18** using [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**1d**)[5b] (0.65 g, 2.09 mmol) and *N*-hydroxysuccinimide (0.24 g, 2.09 mmol). After removing solvent, the residue was purified by column chromatography (hexane/EtOAc; 1:1) to afford pure *cis*-**19** followed by *trans*-**19**.

2.4a *Cis-**19***: Yield 0.572 g (70%); mp 212–216°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.15 (d, $J$ = 6.8 Hz, 1H), 2.73 (s, 4H,), 1.30 (s, 27H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 176.7, 53.4 (d, $J \sim$ 8.0 Hz), 51.3 (d, $J \sim$ 17.0 Hz), 32.6 (d, $J$ = 10.0 Hz), 31.0, 29.5 (d, $J$ = 4.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 90.41, −10.47. IR (KBr, cm$^{-1}$) 3308, 2971, 2934, 2872, 1771, 1721, 1466, 1427, 1395, 1366, 1296, 1213, 1121, 1086, 1034, 1007, 930, 887, 853. HRMS (ESI) calcd. for $C_{16}H_{32}N_4O_3P_2$ $(M + H)^+$ 391.2029, found 391.2028.

2.4b *Trans-**19***: Yield 0.151 g (19%); mp 152–154°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.44 (d, $J$ = 4.8 Hz, 1H), 2.70 (s, 4H), 1.33, 1.30 (2 s, 27H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.3, 53.1 (d, $J \sim$ 6.0 Hz), 52.1 (d, $J \sim$ 16.0 Hz), 32.7 (d, $J$ = 9.0 Hz), 31.0, 25.5. $^{31}$P NMR (162 MHz, $CDCl_3$) δ 73.30 (d, $J$ = 6.4 Hz), −11.15 (d, $J$ = 6.4 Hz). IR (KBr, cm$^{-1}$) 3306, 2973, 2922, 2853, 1740, 1709, 1644, 1470, 1439, 1370, 1292, 1215, 1103, 999, 918, 885, 851. HRMS (ESI) calcd. for $C_{16}H_{32}N_4O_3P_2$ $(M + H)^+$ 391.2029, found: 391.2028.

2.5 *Synthesis of cis [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)-N{-C(= O) − C$_{10}$H$_6$ − C(=O)-}] (cis-**20**)*

Procedure was similar to that for **18** using cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**1d**) [0.35 g, 1.12 mmol], *N*-hydroxy-1,8-naphthalimide (0.239 g, 1.12 mmol) and $NEt_3$ (0.16 mL, 1.12 mmol) The product was isolated by column chromatography (hexane/EtOAc; 1:1) as a pale yellow solid **20**. Yield: 0.375 g (68%); mp: 178–182°C; $^1$H NMR (400 MHz, $CDCl_3$, ppm) δ 8.66 (d, $J$ = 7.6 Hz, 1H, Ar-*H*), 8.59 (d, $J$ = 7.2 Hz, 1H, Ar-*H*), 8.28 (d, $J$ = 3.2 Hz, 1H, Ar-*H*), 8.26 (d, $J$ = 3.2 Hz, 1H, Ar-*H*), 7.82 (t, 1H, Ar-*H*), 7.74 (t, 1H, Ar-*H*), 6.66 (d, $J$ = 7.6 Hz, 1H, *t*−BuN*H*), 1.41 and 1.37 (2 s, 27H, C(C$H_3$)$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 173.0 (1 s, *C* =O), 166.7 (d, $J$ = 7.6 Hz, (C=O)-H-N), 135.4, 134.6, 132.7, 131.6, 131.1, 130.1, 127.8, 127.1, 123.8, 119.1$_3$, 119.1, (Ar-*C*), 53.2 (d, $^2J$(P-C) ∼ 8.0 Hz, *C*(CH$_3$)$_3$), 51.9 (d, $^2J$(P-C) ∼ 18.0 Hz, *C*(CH$_3$)$_3$), 32.2 (d, $^3J$(P-C) = 11.0 Hz, C(*C*H$_3$)$_3$), 31.2 (1 s, C(*C*H$_3$)$_3$). $^{31}$P NMR (160 MHz, $CDCl_3$, ppm) δ 82.10 (1 s, 1P, (*P*-NH*t*-Bu), −8.93 (1 s, 1P, *P*-N). IR (KBr, cm$^{-1}$) 3279, 2969, 2928, 2866, 1676, 1632, 1588, 1559, 1510, 1468, 1372, 1316, 1208, 1142, 1092, 1038, 1011, 943, 880, 762. HRMS (ESI) calcd for $C_{24}H_{34}N_4O_3P_2$ $(M + H)^+$ 489.2185, found 489.2184.

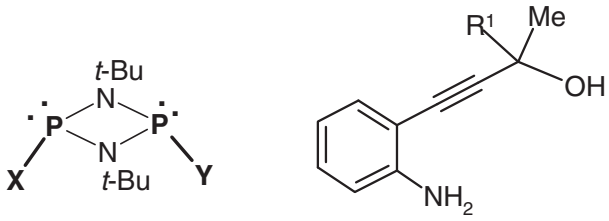
2.6 *X-ray structural analysis of **14**, cis-**18**, trans-**18**, and cis-**19***

Single crystal X-ray diffraction data for compounds **14** and *trans*-**18** were collected on an OXFORD diffractometer and that for, *cis*-**18**, and *cis*-**19** were collected on a Bruker AXS-SMART diffractometer using Mo K$_\alpha$ (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[17] The data for compounds **14** and *trans*-**18** were not good due to poor quality of the crystals, although the structures refined well. Full details of the X-ray structure solution and refinement as a CIF file are available as Supplementary Information.

2.6a *Compound **14***: colourless needles, $C_{28}H_{42}Br_2N_4OP_2$, $M$ = 512.60, Monoclinic, Space group $P2_1/c$, $a$ = 13.4400(19), $b$ = 17.383(2), $c$ = 13.2418(17) Å, $\beta$ = 104.546(13), $V$ = 2994.5(7) Å$^3$, $Z$ = 4, $\mu$ = 0.171 mm$^{-1}$, data/restraints/parameters: 4580/1/332, R indices (I >2σ(I)): R1 = 0.1372, *w*R2 (all data) = 0.2844. The reflections were weak and the quality of the data was only moderate (hence an A alert was shown in checkcif), but good enough to fully refine the structure. Attempts to obtain better crystals were not successful. CCDC No. 1016234.

2.6b *Cis-**18***: colourless block, $C_{24}H_{26}N_4O_6P_2$, $M$ = 528.43, Monoclinic, Space group $C2/c$, $a$ = 21.035(4), $b$ = 10.233(2), $c$ = 15.523(3) Å, $\beta$ = 128.87(3), $V$ = 2601.4(9) Å$^3$, $Z$ = 4, $\mu$ = 0.213 mm$^{-1}$, data/restraints/parameters: 2294/0/166, R indices (I > 2σ(I)): R1 = 0.0411, *w*R2 (all data) = 0.1091. CCDC No. 927548.

2.6c *Trans-**18***: colourless block, $C_{25}H_{28}N_4O_6P_2Cl_2$, $M$ = 613.35, Triclinic, Space group $P\bar{1}$, $a$ = 7.9645(14), $b$ = 9.0060(12), $c$ = 22.375(3) Å, $\alpha$ = 95.477(11), $\beta$ = 93.033(13), $\gamma$ = 113.752(15), $V$ = 1454.9(4) Å$^3$, $Z$ = 2, $\mu$ = 0.379 mm$^{-1}$, data/restraints/parameters: 5019/0/359, R indices (I > 2σ(I)): R1 = 0.1331, *w*R2 (all data) = 0.2994. CCDC No. 927549.




X , Y = NH-*t*-Bu (**1a**)
NH-*i*-Pr (**1b**)
Cl (**1c**)
X = Cl, Y = NH-*t*-Bu (**1d**)

R1 = Ph (**13a**)
R1 = Me (**13b**)
R1 = H (**13c**)

**Chart 2.** Cyclodiphosphazane precursors **1a–d** and propargyl alcohols **13a–c** used in this study.

The reflections were weak and the quality of the data was only moderate, but good enough to fully refine the structure.

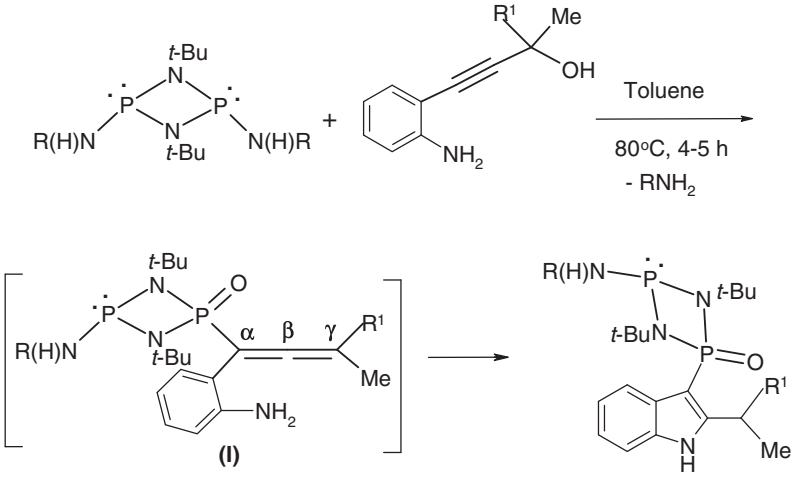
2.6d *cis-**19***: colourless block, $C_{16}H_{32}N_4O_3P_2$, $M = 390.40$, Monoclinic, Space group $P2_1/c$, $a = 18.116(4)$, $b = 10.276(2)$, $c = 11.554(2)$ Å, $\beta = 90.29(3)$, $V = 2150.7(7)$ Å$^3$, $Z = 4$, $\mu = 0.223$ mm$^{-1}$, data/restraints/parameters: 3629/0/262, R indices ($I > 2\sigma(I)$): R1 = 0.0740, *w*R2 (all data) = 0.1505. CCDC No. 927550.

## 3. Results and Discussion

Cyclophosphazane precursors used in this study are [XP($\mu$-N-*t*-Bu)$_2$PY] [X = Y = NH-*t*-Bu (**1a**);[5c] X = Y = NH-*i*-Pr (**1b**);[5c] X = Y = Cl (**1c**);[16] X = Cl, Y = NH-*t*-Bu (**1d**)].[5b] *o*-Amino functionalized propargyl alcohols **(13a–c**) were prepared from 2-iodo aniline and the corresponding propargyl alcohols by following standard procedures.[15] These are shown in chart 2. We shall first discuss the reaction with propargyl alcohols followed by those with *N*-hydroxyphthalimide/*N*-hydroxy succinimide/*N*-hydroxy-1,8-naphthalimide.

### 3.1 *Reactivity of [(RNH)P($\mu$-N-t-Bu)]$_2$ [R =t-Bu (**1a**), i-Pr (**1b**)] towards functionalized propargylic alcohols **13a–c***

Initially, we treated the cyclodiphosphazanes [(RNH)P($\mu$-N-*t*-Bu)]$_2$ [R = *t*-Bu (**1a**), *i*-Pr (**1b**)] with the aryl-substituted propargyl alcohol **13a**[15] possessing *o*-amino group. This led to cyclodiphosphazane-based substituted indoles **14** and **15** shown in scheme 2. These compounds are formed essentially as single products, but the solubility in organic solvents is rather poor. Here, the cyclodiphosphazane reacts with the propargyl alcohol forming the cyclodiphosphazane-based allene intermediate **I**[8,12] that undergoes cyclization by the attack of -NH$_2$ functionality on the $\beta$-carbon of the allene leading to the substituted cyclodiphosphazane-based indole. The IR spectra of **14** and **15** show the expected $\nu$(NH) band in the region 3353-3381 cm$^{-1}$. In the $^1$H NMR spectrum of **14**, the *t*-BuN*H* and indole-N*H* peaks appear at $\delta$ 3.32 and 8.28, respectively. The corresponding signals for **15** appear at $\delta$ 3.01 and 8.50, respectively. The $^{31}$P NMR spectra of **14** shows two doublets at $\delta$ 10.7 and 78.0 with $^2J$(PP) of 10.0 Hz. In the case of **15**, the broad signals appear at $\delta$ 10.5



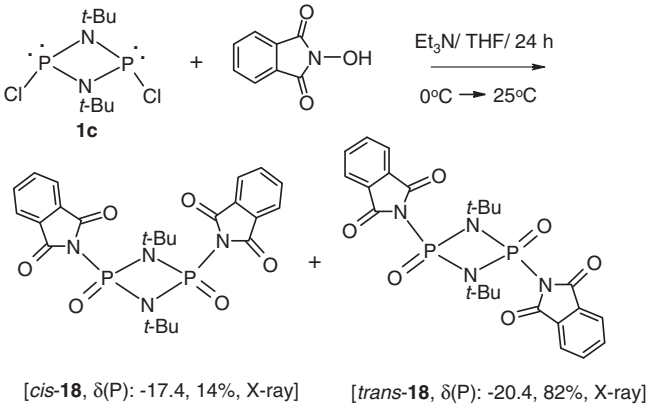

R = *t*-Bu, R$^1$ = Ph [**14**, δ(P): 10.7, 78.0; 92%, X-ray]
R = *i*-Pr, R$^1$ = Ph [**15**, δ(P): 10.5, 82.7; 81%]
R = *t*-Bu, R$^1$ = Me [**16**, δ(P): 13.5, 78.5; 90%]
R = *t*-Bu, R$^1$ = H [**17**, δ(P): 17.5, 82.6; 88%]

**Scheme 2.** Formation of cyclodiphosphazane-based indoles **14**–**17**.

and 82.7. In the $^{13}$C NMR spectra, the $^{1}J$(P-C) value of 172.0 Hz [$\delta$(C) $\sim$ 102] for **14** and **15** suggests that the corresponding phosphorus is connected to an sp$^2$ carbon.[5c] All these data are consistent with the structures shown in scheme 2. Compounds **16** and **17** were prepared similarly by using the cyclodiphosphazane (**1a**) and propargyl alcohols **13b** and **13c**, respectively. The structure of compound **14** was further confirmed by single crystal X-ray diffraction (figure 1). Although the quality of X-ray data was only moderate, complete refinement could be effected and the formation of the P-C bond as well as the indole ring can be clearly seen. Of the two isomers possible, the one in which indolyl group on one phosphorus is *trans* to the -NHR group on the second phosphorus is formed in the reaction.

### 3.2 *Reactivity of [ClP-N(t-Bu)]$_2$(**1c**) and [(t-BuNH)P($\mu$-N-t-Bu)$_2$P-Cl] (**1d**) towards N-hydroxy derivatives*

This part of the study initially was aimed at rationalizing the reaction of P$^{III}$ substrates with nitrofuntionalized propargyl alcohols from our group, wherein a P$^{III}$-O-N to P$^{V}$(O)-N rearrangement was implicated.[12] Here, we present a more detailed study on this aspect. Thus, we treated the cyclodiphosphazane [ClP-N(*t*-Bu)]$_2$ (**1c**) with *N*-hydroxy phthalimide/Et$_3$N and obtained the novel rearranged products *cis*-**18** and *trans*-**18** as shown in scheme 3. These compounds are formed by the substitution of a -Cl group by the *N*-hydroxyl reactant, followed by P$^{III}$-O-N $\rightarrow$ P$^{V}$(O)-N rearrangement. To our knowledge, such reactions are never reported in cyclodiphosphazane chemistry prior to our study. In the reaction mixture, *trans*-**18** is the major product and *cis*-**18** is the minor product. The $^{31}$P NMR spectra of *cis*-**18** and *trans*-**18** show signals at $-17.4$, and $-20.4$, respectively. This small difference [$\Delta\delta$ $\sim$ 3 ppm] in the $^{31}$P NMR chemical shift values may be contrasted with the huge difference in the chemical shift values observed for *cis*- and *trans*-amino-substituted cyclodiphosph(III)azanes [$\Delta\delta$ $\sim$ 90 ppm].[18] The structures of these two compounds are further confirmed by X-ray crystallography (figures 2 and 3).




**Scheme 3.** Reaction of *N*-hydroxyphthalimide with **1c** leading to P–N-substituted products *cis*-**18** and *trans*-**18**.

In an effort to probe whether there is any special preference for either of the isomers, *cis* or *trans*, we treated the chloro-substrate [(*t*-BuNH)P($\mu$-N-*t*-Bu)$_2$P-Cl] (**1d**) with *N*-hydroxy succinimide. Here, we could isolate both the rearranged products *cis*-**19** and *trans*-**19** (scheme 4; *cis* and *trans* of exocyclic P-N bonds

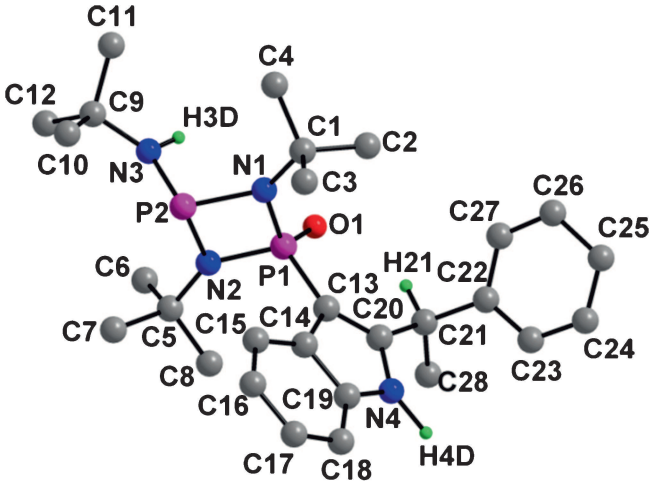



**Figure 1.** Molecular structure of compound **14**. Hydrogen atoms (except NH and CH) are omitted for clarity. Selected bond parameters: P1-C13 1.766(9), C13-C14 1.462(11), C13-C20 1.351(12), C20-C21 1.525(13), C20-N4 1.384(11) (Å).

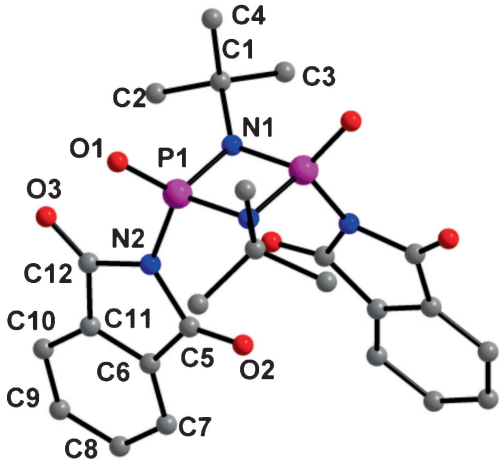



**Figure 2.** Molecular structure of *cis*-**18**. Hydrogen atoms are omitted for clarity. One identical half molecule present in the asymmetric unit. Selected bond distances: P1-N1 1.673(2), P1-N2 1.706(2), P1-O1 1.450(1) (Å).

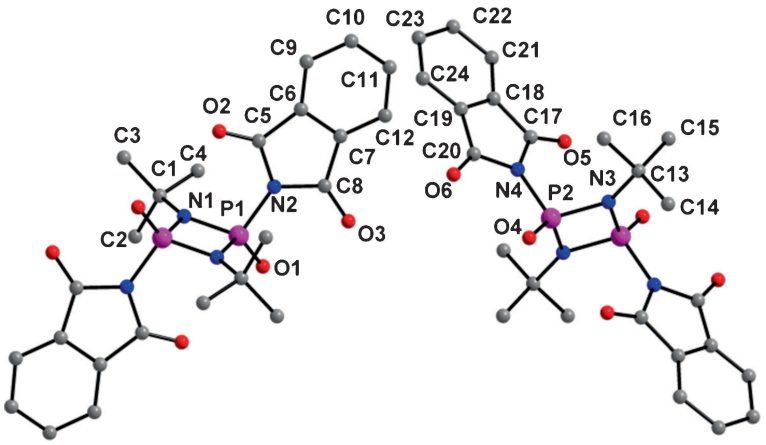
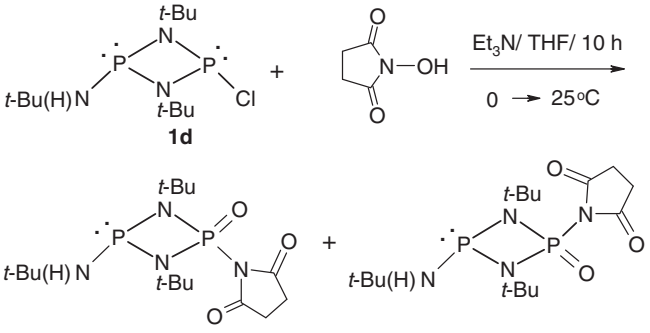



**Figure 3.** Molecular structure of compound *trans*-**18** 1/2CH2Cl2. Hydrogen atoms and the solvent molecule are omitted for clarity. Two essentially identical half molecules in the asymmetric unit are present. Selected bond parameters: P1-N1 1.643(6), P1-N2 1.708(7), P1-O1 1.451(6), P2-N3 1.679(7), P2-N4 1.713(7), P2-O4 1.443(6) (Å).

with respect to the cyclophosphazane ring) in yields of 70% and 19%, respectively. This result shows that one isomer is predominant, but a direct comparison to *cis*-**18** and *trans*-**18** may not be appropriate because in the case of *cis*-**19** and *trans*-**19**, only one phosphorus end has reacted with *N*-hydroxysuccinimide. The $^{31}$P NMR spectra of *cis*-**19** and *trans*-**19** show two signals each at [−10.5, 90.4] and [−11.2, 73.3], respectively, which suggests that the two isomers are readily distinguishable in the P$^{III}$ region. We were able to obtain single crystals suitable for X-ray structure studies only in the case of *cis*-**19**. Compound *cis*-**19** shows intra-molecular hydrogen bonding between N(3)H and C(13)=O(2) (figure 4). This feature could be a driving force for the predominance of isomer with this configuration.

We treated *N*-hydroxy-1,8-naphthalimide with cyclodiphosphazane [ClP-N(*t*-Bu)]$_2$ (**1c**) also, but we could not effect the reaction under these conditions However, the cyclodiphosphazane [(*t*-BuNH)P($\mu$-N-*t*-Bu)$_2$P-Cl] (**1d**) afforded *cis*-**20** shown in scheme 5. The IR spectrum of *cis*-**20** shows the $\nu$(NH) band at 3279 cm$^{-1}$. The $^{31}$P NMR spectrum shows two signals at $\delta$−8.9 and 82.1 [$^2J$(PP) < 3 Hz] as expected. The $^1$H NMR spectrum of *cis*-**20** shows the *t*-BuN*H* peak at $\delta$ 6.70. It may be noted that the *t*-BuN*H* peak for *cis*-**19** [$\delta$ 5.15] is much downfield compared to that for *trans*-**19** [$\delta$ 3.44]. On this basis, we have assigned a *cis*-stereochemistry for compound **20**. The assignment of *cis*-stereochemistry for **20** is also consistent with the fact that analogous reaction of **1d** with *N*-hydroxysuccinimide led to *cis*-**19** as the major product. The observation that **1c** failed to react, but **1d** reacted




**Scheme 4.** Reaction of N-hydroxysuccinimide with **1d** leading to P-N-subsitituted products *cis*-**19** and *trans*-**19**.

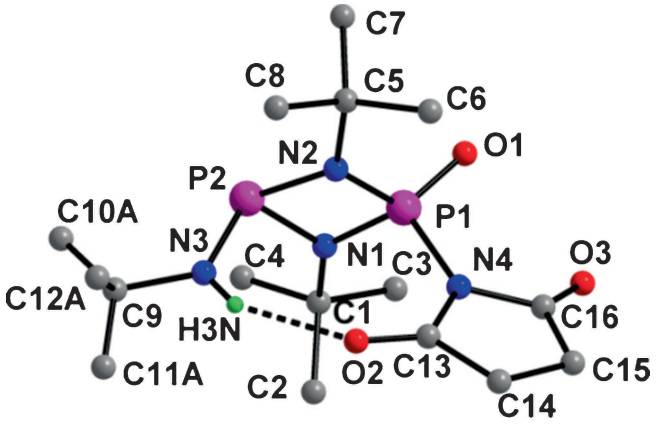
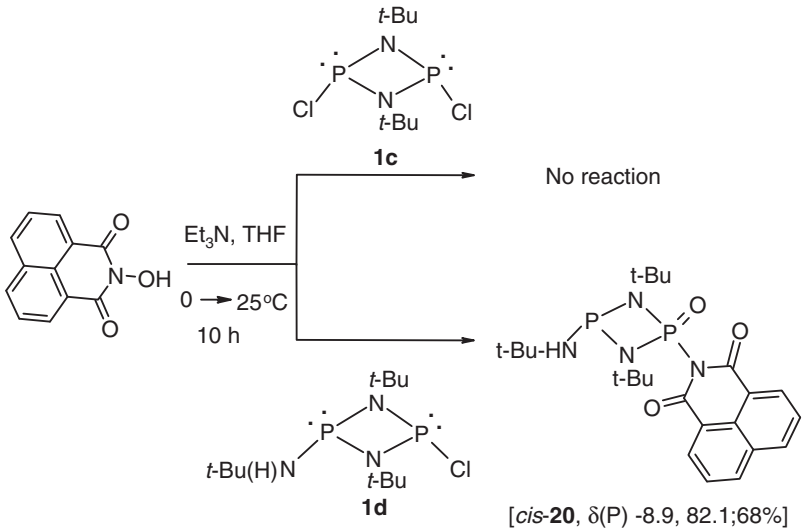



**Figure 4.** Molecular structure of compound *cis*-**19**. For the disordered t-butyl group at C9; only one position for the methyl groups is shown. Hydrogen atoms (except NH) are omitted for clarity. Hydrogen bond parameters: N3-H3N. . .O2 0.80(4) 2.17(4) 2.902(4) Å, 154(4)°.



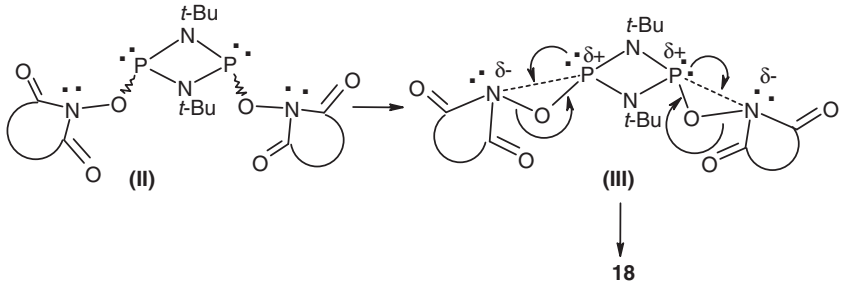

**Scheme 5.** Reaction of *N*-hydroxy-1,8-naphthalimide with **1d** leading to P-N-subsitituted product *cis*-**20**.

with *N*-hydroxy-1,8-naphthalimide may be linked to electronic factors. We have not probed this aspect further.

As regards the formation of products *cis*-**18** and *trans*-**18**, involvement of intermediates **II-III** may be invoked (scheme 6). Rearrangement of the three-membered ring containing phosphonium betaine **III** will lead to compounds *cis*-**18** and *trans*-**18**. In a similar manner, formation of compounds **19** and **20** may be rationalized. It may be noted that the phosphonium intermediate resulting from **III** bears some resemblance to the one proposed in Arbuzov rearrangement. However, no additional reagent similar to alkyl halide is used in our rearrangement. Formation of *cis* or *trans* isomers may be linked to the relative disposition of the substituents in the $P^{III}$ intermediate **II**.

### 3.3 *Brief comments on the structural aspects*

The P-N bond distances and selected angles in the compounds studied by X-ray crystallography along with analogous compounds **21-24** (chart 3) reported by us[12] are tabulated in table 1. $P^{III}$-N(ring) distances are always longer than the $P^{V}$-N(ring) distances. However, exocyclic $P^{V}$-N distances are longer than the corresponding $P^{III}$-N distances in all the cyclodiphosphazane derivatives. This feature suggests a competition for the bonding electrons. The endocyclic N-$P^{III}$-N angle is, in general, smaller than that of endocyclic N-$P^{V}$-N angle probably due to (i) the lone pair of electrons on $P^{III}$, which tries to occupy more space, and (ii) the greater contribution from $\sim sp^3$ hybridization at the $P^{V}$ centre. This feature could have forced the $P^{III}$-N(ring) distance to be longer. The $P^{V}$-N exocyclic distances are comparable to the apical P-N bonds in pentacoordinate phosphoranes[19] and are slightly shorter than the expected P-N (single) bond distances based on Schomaker–Stevenson empirical expression (1.77 Å).[20] The ring nitrogen atoms are essentially planar with the sum of the bond angles at nitrogen close to 360°. The four-membered $P_2N_2$ ring in compounds *cis*-**18**, *trans*-**18** and **23** is planar, but in other cases, deviations do occur to an extent of 0.03–0.06 Å from the mean plane.




**Scheme 6.** Possible pathway for the $P^{III}$-O-N → $P^{V}$(O)-N rearrangement.

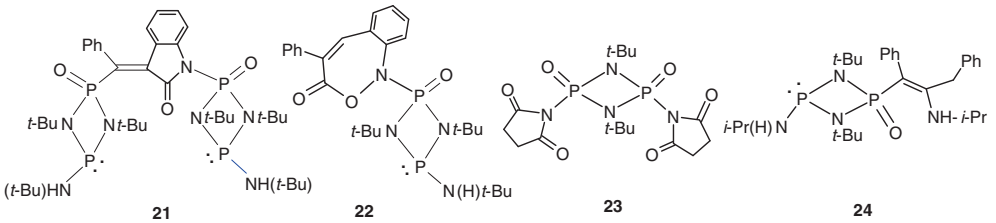



**Chart 3.** Selected compounds from ref.[12].

**Table 1.** Comparison of P-N bond parameters in cyclodiphosphazane derivatives.

| Compound | $P^V$-N(ring) | $P^{III}$-N(ring) | $P^V$-N(exo) | $P^{III}$-N(exo) | N-$P^V$-N(ring) | N-$P^{III}$-P(ring) |
|---|---|---|---|---|---|---|
| **12**· 1/2$H_2O$ (ref. [12]) | 1.649(4) | 1.743(5) | | 1.662(5) | 85.2(2) | 79.1(2) |
| | 1.649(5) | 1.760(4) | | 1.654(5) | 86.0(2) | 79.0(2) |
| | 1.643(5) | 1.752(4) | | | | |
| | 1.639(4) | 1.767(5) | | | | |
| **14** (Present study) | 1.652(7) | 1.749(9) | - | 1.642(9) | 85.2(4) | 79.2(4) |
| | 1.636(8) | 1.744(8) | | | | |
| *Cis*-**18** (Present study) | 1.673(2) | | 1.706(2) | | 85.3(1) | |
| | 1.655(2) | | | | | |
| *Trans*-**18**·1/2$CH_2Cl_2$ (Present study) | 1.643(6) | 1.708(7) | | | 84.5(3), | |
| | 1.672(6) | 1.713(7) | | | 86.1(4) | |
| | 1.679(7) | | | | | |
| | 1.670(7) | | | | | |
| *cis*-**19** | 1.626(3) | 1.750(3) | 1.738(3) | 1.638(3). | 86.5(2) | 79.3(1) |
| | 1.631(3) | 1.747(3) | | | | |
| **21** (ref. [12]) | 1.644(3) | 1.750(3) | 1.716(3) | 1.663(3) | 85.7(1) | 78.9(1) |
| | 1.642(3) | 1.763(3) | | 1.646(3) | 86.6(1) | 79.0(1) |
| | 1.634(3) | 1.769(3) | | | | |
| | 1.631(3) | 1.752(3) | | | | |
| **22**· $PhCH_3$ (ref. [12]) | 1.652(4) | 1.736(4) | 1.697(3) | 1.642(4) | 85.3(2) | 79.5(2) |
| | 1.639(3) | 1.736(4) | | | | |
| **23** (ref. [12]) | 1.667(2) | 1.705(2) | | | 85.5(1) | - |
| | 1.650(2) | | | | | |
| **24**·1/2$H_2O$ (ref. [12]) | 1.658(2) | 1.743(2) | | 1.653(2) | 84.9(1) | 79.7(1) |
| | 1.652(2) | 1.741(2) | | | | |

## 4. Summary

We have developed a straightforward route to synthesize cyclophosphazane-based indoles starting from *ortho*-amino functionalized propargyl alcohols via allene intermediates. We have isolated these indoles directly from the reaction mixture without performing column chromatography. We have also synthesized novel P-N bonded compounds using cyclodiphosphazanes and *N*-hydroxy substrates which involve a rearrangement from $P^{III}$-O-N to $P^V$(O)–N, a feature previously not reported in cyclophosphazane chemistry.

## Supplementary Information

The electronic supporting information (CIF file containing the details of crystal structures of compounds reported in this work) and selected NMR data (figures S1–S4) can be seen in www.ias.ac.in/chemsci.

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