

Mono- and di-substituted urea derivatives of cyclodiphosphazane: $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{PN}(\text{Me})\text{CON}(\text{H})\text{Me}]$ and $[\text{Me}(\text{H})\text{NCON}(\text{Me})\text{P}(\mu\text{-N}^t\text{Bu})_2]$

Devarajan Suresh,^a Maravanji S. Balakrishna^{a,*} and Joel T. Mague^b

^aPhosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India

^bDepartment of Chemistry, Tulane University, New Orleans, LA 70118, USA

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Abstract—The reaction of *cis*- $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2]$ with *N,N'*-dimethylurea leads to the formation of both mono- and di-substituted derivatives $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{NMeCON}(\text{H})\text{Me})]$ and $[(\mu\text{-N}^t\text{Bu})\text{P}(\text{NMeCON}(\text{H})\text{Me})_2]$, instead of monomeric, dimeric or higher oligomeric macrocycles. The structure of $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{NMeCON}(\text{H})\text{Me})]$ shows rare non-bonded $\text{P} \cdots \text{Cl}$ and intermolecular hydrogen bonding interactions leading to a 2D-sheet like structure.

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The renewed interest in the chemistry of cyclodiphosphazanes in recent years is partly due to the utilization of robust P_2N_2 skeletons as building blocks to make a variety of cages¹ and macrocycles² besides their interesting ligating behavior both as neutral³ and anionic ligands.⁴ The reactions between $[\text{CIP}(\mu\text{-NR})_2]$ ($\text{R} = \text{alkyl}$, aryl) and di- or polyfunctional alcohols, amines, or amino-alcohols resulted in the formation of simple monomeric derivatives⁵ and/or dimeric-^{2a} to pentameric macrocycles.^{2c,d} Only a very few reactions have yielded mono- and/or di-substituted derivatives (Chart 1) containing appended amine or alcohol functionalities,⁶ which can serve as valuable hybrid ligands for catalytic

applications or as synthons for supramolecular chemistry.

This may be due to the reactivity of $\text{P}-\text{Cl}$ bonds and the stoichiometry involved in the reactions. Interestingly, in the reactions of $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2]$ with various diols and diamines, the presence of an excess of nucleophile resulted in the formation of higher oligomers⁷ but not compounds of type **I** or **II** except for an amino derivative (type **II**) reported recently.⁶ Further, there are no reports of cyclodiphosphazanes containing exocyclic functionalities except for the bis(amido)derivatives which have been studied extensively.^{4a,b} This prompted us to investigate the substitution reactions of cyclodiphosphazanes with different nucleophiles other than the usual diols or diamines to make derivatives of type **I** and **II**. Herein, we describe the reaction of *N,N'*-dimethylurea with the cyclodiphosphazane $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2]$, which resulted in the isolation of both mono- and di-substituted derivatives. A binuclear gold(I) complex of **3** and the X-ray structure of **2** are also described.

The reaction of *cis*- $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2]$ **1** with 1 equiv of *N,N'*-dimethylurea in the presence of 1 equiv of triethylamine at -78°C afforded the mono-substituted derivative⁹ $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2\text{P}(\text{NMeCON}(\text{H})\text{Me})]$ **2** in 55% yield along with a small quantity of the di-substituted derivative $[(\mu\text{-N}^t\text{Bu})\text{P}(\text{NMeCON}(\text{H})\text{Me})_2]$ **3** (10%), which were separated by fractional crystallization. A similar

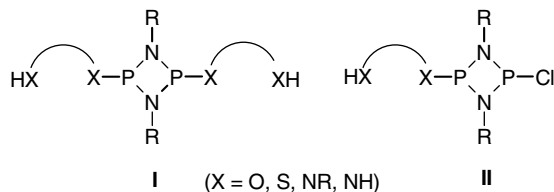


Chart 1.

Keywords: Cyclodiphosphazanes; Urea derivatives; $\text{P} \cdots \text{Cl}$ Interactions.

* Corresponding author. Tel.: +91 22 2574 7181; fax: +91 22 2572 3480; e-mail: krishna@chem.iitb.ac.in

reaction of **1** with 2 equiv of *N,N'*-dimethylurea in THF at 0 °C resulted in the exclusive formation of **3** in 65% yield.¹⁰ The ³¹P NMR spectrum of **2** shows two doublets at 188.1 and 120.5 ppm, respectively, for the P(Cl) and P(NMe(CON(H)Me) centers with a ²J_{PP} coupling of 32.3 Hz. The ¹H NMR spectrum shows two resonances for the NMe groups at 2.86 ppm (doublet, ³J_{PH} = 1.6 Hz) and 2.7 (singlet) ppm indicating the mono-substituted nature of **2**. The resonance due to the NH protons appeared at 5.80 ppm. The ³¹P NMR spectrum of **3** shows a single resonance at 69.4 ppm and the proton NMR spectral data were consistent with the structure proposed. Further evidence for the structural composition was obtained from the microanalytical data. The structure of **2** was confirmed by X-ray diffraction studies.¹¹ Compound **2** crystallizes in the orthorhombic space group *P*2₁2₁2₁ (Fig. 1a). The P₂N₂ ring is slightly puckered with a puckering parameter of 0.161 Å. The dihedral angle between the P1,N1,N2 plane and the N1,P2,N2 plane is 165.68° while that between the P1,N1,P2 plane and the P1,P2,N2 plane is 163.47°. The phosphorus substituents are in a mutually *cis*-disposition. The P1 center and the N3–C10–N4 fragment are in a semilunar arrangement with the N3–C10–N4 plane (urea fragment) orthogonal to the P₂N₂ ring bond. The exocyclic NH protons show weak intermolecular hydrogen bonding interactions with the carbonyl oxygen from the adjacent molecule (N–H···O = 138.5°; H···O = 2.392 Å) (Fig. 1b), whereas the chlorine atom links weakly to the adjacent chlorine bound phosphorus (P–Cl···P = 133.15° and Cl···P = 3.485 Å) to give a 2D-sheet like structure as shown in Figure 1c.

The P···Cl distance of 3.485 Å is within the sum of the van der Waals radii (3.55 Å)¹² and is shorter than the corresponding distance found in the previously reported cyclotriphosphazane [PCINeT]₃.¹³ The P2–N bond distances are slightly shorter than the P1–N bond distances by 0.044 Å and this may be due to the presence of the chlorine atom on P2 which makes it a better π-acceptor than the urea bound P1 center.

In a preliminary study, the reaction between **3** and AuCl(SMe₂) in dichloromethane resulted in the formation of a binuclear gold(I) complex,¹⁴ *cis*-[MeNHC(O)-NMeP(μ-*N'*Bu)AuCl]₂ **4** with the ligand exhibiting a bridging mode of coordination. The ³¹P NMR spectrum of **4** shows a single resonance at 80.5 ppm with a coordination shift of 11 ppm.

In summary, the reaction between the dichlorocyclodiphosphazane *cis*-[CIP(μ-*N'*Bu)]₂ and *N,N'*-dimethylurea yielded both mono- and disubstituted derivatives and not the expected monomeric or dimeric to pentameric derivatives as observed previously. These products are particularly interesting as ligands to bring both low-valent platinum metals and high-valent early metals into one molecule, these are species which are of great interest in catalysis and supramolecular chemistry. Work in this direction is under active investigation in our laboratory.

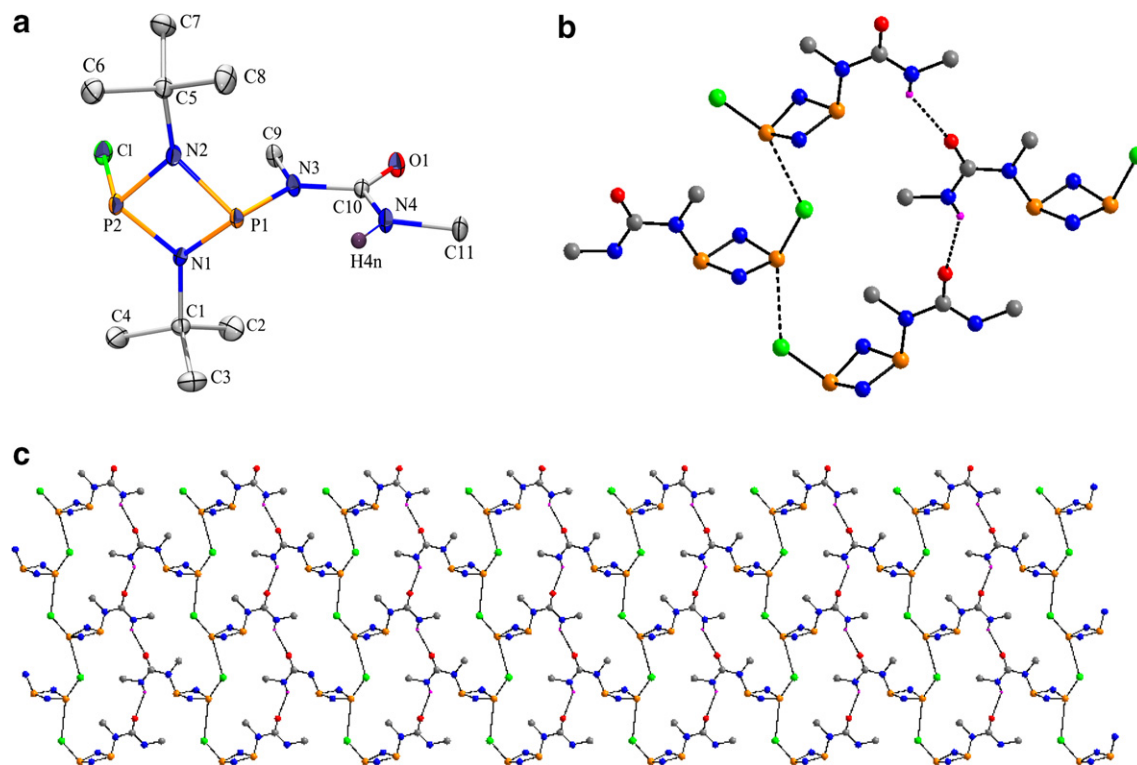


Figure 1. (a) Molecular structure of **2**. For clarity all hydrogen (except H4n–N4) atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. (b) Showing intermolecular N–H···O and P–Cl···P interactions. (c) 2D Sheet like arrangement of molecules **2** in the crystal lattice. Selected bond lengths (Å): Cl–P2, 2.200(1); P1–N1, 1.730(2); P1–N2, 1.723(2); P2–N1, 1.686(2); P2–N2, 1.687(2); P1–N3, 1.700(1); O1–C10, 1.224(2). Selected bond angles (°): N1–P1–N2, 80.11(8); N1–P1–N3, 104.94(9); N2–P1–N3, 106.21(9); Cl–P2–N1, 105.29(7); Cl–P2–N2, 105.00(7); N1–P2–N2, 82.42(8).

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- Synthesis of compound 2:** A mixture of *N,N'*-dimethylurea (160 mg, 1.82 mmol) and triethylamine (190 mg, 1.87 mmol) in 20 ml of THF was added dropwise over a period of 20 min to a well stirred THF solution (20 ml) of [CIP(μ -*N'*Bu)]₂ (510 mg, 1.85 mmol) at -78°C . Immediately upon addition, a white precipitate of Et₃N·HCl was formed. The reaction mixture was brought to room temperature and stirring was continued for 18 h. All the volatiles were removed under vacuum. The residue was extracted with toluene and Et₃N·HCl was filtered off. The filtrate was concentrated under reduced pressure to 10 ml and kept at -25°C to afford colorless crystals of **2**. Yield: 55% (332 mg, 1.02 mmol). Mp: 122–124 $^\circ\text{C}$. ¹H NMR (400 MHz, CDCl₃): δ 5.80 (br s, 1H, *NH*), 2.86 (d, ³J_{PH} = 1.6 Hz, 3H, *CH*₃), 2.77 (s, 3H, *CH*₃), 1.35 (s, 18H, *t*Bu). ³¹P {¹H} NMR (161.8 MHz, CDCl₃): δ 188.1 (d, ²J_{PP} = 32.3 Hz), 120.5 (d, ²J_{PP} = 32.3 Hz). Anal. Calcd for C₁₁H₂₅ClN₄OP₂: C, 40.43; H, 7.71; N, 17.14. Found: C, 40.88; H, 7.92; N, 17.62.
- Synthesis of compound 3:** A mixture of *N,N'*-dimethylurea (430 mg, 4.88 mmol) and triethylamine (490 mg, 4.84 mmol) in 25 ml of THF was added dropwise over a period of 20 min to a well stirred solution of [CIP(μ -*N'*Bu)]₂ (660 mg, 2.39 mmol) in THF (20 ml) at 0°C . The reaction mixture was brought to room temperature and stirred for 22 h. All the volatiles were removed under reduced pressure and the residue obtained was extracted with toluene and Et₃N·HCl was filtered off. The filtrate was concentrated to a small volume (10 ml) and stored at -25°C to give colorless crystals of **3**. Yield: 65% (590 mg, 1.55 mmol). Mp: 138–140 $^\circ\text{C}$. ¹H NMR (400 MHz, CDCl₃): δ 5.75 (br s, 2H, *NH*), 2.86 (d, ³J_{PH} = 1.6 Hz, 6H, *CH*₃), 2.76 (s, 6H, *CH*₃), 1.34 (s, 18H, *t*Bu). ³¹P {¹H} NMR (161.8 MHz, CDCl₃): δ 69.4 (s). FT-IR (CHCl₃): ν_{NH} 3381(b) cm⁻¹, ν_{CO} 1654 (s) cm⁻¹. Anal. Calcd for C₁₄H₃₂N₆O₂P₂: C, 44.43; H, 8.52; N, 22.21. Found: C, 43.77; H, 8.86; N, 21.45.
- Crystal data for 2:** C₁₁H₂₅N₄OClP₂, *M*_w = 326.74, orthorhombic, *P*2₁2₁2₁, *a* = 10.3726(6) Å, *b* = 11.5708(7) Å, *c* = 13.7242(9) Å, *V* = 1647.17(18) Å³, *Z* = 4, *D*_c = 1.318 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 0.425 mm⁻¹, *F*(000) = 696, GOF = 1.04, *T* = 293 K. Data were collected on a Bruker Smart APEX CCD diffractometer using Mo K α radiation. A total of 14,705 reflections (2.30 < 2 θ < 28.3) were processed of which 3963 were unique (*R*_{int} = 0.030). The final *wR*₂ value was 0.0940 (all data) and *R*₁ = 0.0366 [*I* > 2 σ (*I*)]. CCDC Ref. No. 630668.
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- Synthesis of complex 4:** A solution of [ClAu(SMe₂)] (34.2 mg, 11.6 μmol) in CH₂Cl₂ (5 ml) was added dropwise to a CH₂Cl₂ solution (5 ml) of *cis*-[MeNHCO(NMeP(μ -*N'*Bu)]₂ (22.0 mg, 5.8 μmol) at room temperature. The reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure and the residue washed with ether to afford **4** as a colorless crystalline solid. Yield: 75% (36.7 mg, 4.35 μmol). Mp: 150–152 (dec) $^\circ\text{C}$. ¹H NMR (400 MHz, CDCl₃): δ 5.64 (br s, 2H, *NH*), 3.43 (d, ³J_{PH} = 15.6 Hz, 6H, *CH*₃), 2.83 (s, 6H *CH*₃), 1.56 (s, 18H, *t*Bu). ³¹P {¹H} NMR (400 MHz, CDCl₃): δ 80.5 (s). FT-IR (CHCl₃): ν_{NH} 3354 (b) cm⁻¹, ν_{CO} 1652 (s) cm⁻¹. Anal. Calcd For C₁₄H₃₂Au₂Cl₂N₆O₂P₂: C, 19.94; H, 3.82; N, 9.96. Found: C, 19.48; H, 4.23; N, 9.16.