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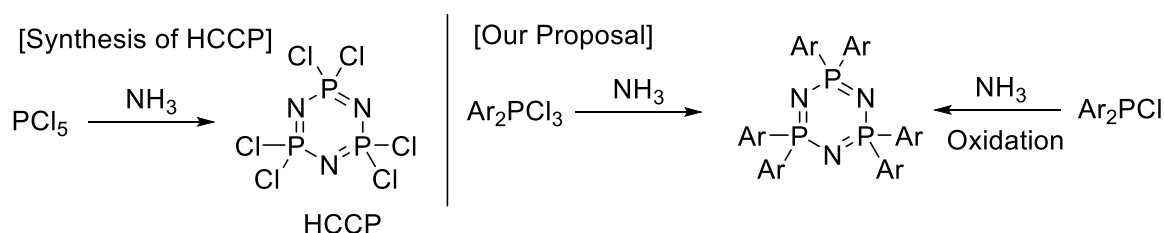
ELECTROOXIDATION OF CHLORODIPHENYLPHOSPHINE UNDER AMMONIA ATMOSPHERE. SYNTHESIS OF 2,2,4,4,6,6-HEXAPHENYLCYCLOTRIPHOSHAZENE AND IMINOBIS(AMINODIPHENYLPHOSPHORUS) CHLORIDE

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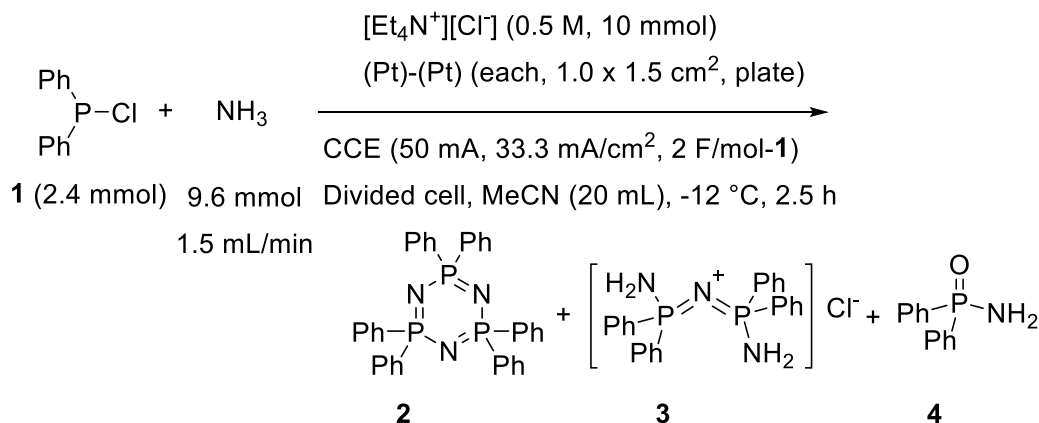
Abstract – Electrooxidation of MeCN solution of chlorodiphenylphosphine in the presence of Cl^- under NH_3 atmosphere gave a mixture of 2,2,4,4,6,6-hexaphenylcyclotriphosphazene and iminobis(aminodiphenylphosphorus) chloride.

Cyclotriphosphazene has a 6-membered heterocyclic ring in which three P atoms and three N atoms are alternately connected. Hexaarylcyclotriphosphazene $[(\text{Ar}_2\text{PN})_3]$ was investigated as a host materials in blue phosphorescent organic light-emitting diodes.¹ $[(\text{Ar}_2\text{PN})_3]$ was prepared by 1) reaction of $[(\text{Cl}_2\text{PN})_3]$ and ArMgBr^2 or 2) reaction of $\text{Ar}_2\text{P}(=\text{O})\text{NH}_2$ and $\text{PPh}_3/\text{CCl}_4$.¹ However, the former reaction needs 2 weeks for completion, and the latter needs CCl_4 which has heavy environmental impact. Since hexachlorocyclotriphosphazene $[(\text{Cl}_2\text{PN})_3]$, HCCP is industrially synthesized from PCl_5 and NH_4Cl ,³ $[(\text{Ar}_2\text{PN})_3]$ may be produced from a reaction of Ar_2PCl_3 and NH_3 or $\text{Ar}_2\text{P}(\text{Cl})$ and NH_3 under oxidation conditions (Scheme 1).



Scheme 1. Preparation of Cyclotriphosphazenes

We investigated electrooxidation of $\text{Ph}_2\text{P-Cl}$ (**1**) and NH_3 in acetonitrile in the presence of chloride ion to find that a mixture of 2,2,4,4,6,6-hexaphenylcyclotriphosphazene $[(\text{Ph}_2\text{PN})_3]$, **2** and iminobis(aminodiphenylphosphorus) chloride $[(\text{NH}_2\text{PAR}_2)_2\text{N}^+]\text{Cl}^-$, **3** was obtained (Scheme 2).



Scheme 2. Reaction of $\text{Ph}_2\text{P-Cl}$ and NH_3 under electrooxidation conditions

The typical procedure was as follows. The electrolysis was carried out in a divided cell equipped with magnetic stirring bars and Pt electrodes ($1.5 \times 1.0 \text{ cm}^2$) (Figure 1). In the anodic chamber was placed a MeCN (10 mL) solution of $[\text{Et}_4\text{N}^+][\text{Cl}^-]$ (830.8 mg, 5.01 mmol, 0.51 M) and $\text{Ph}_2\text{P-Cl}$ (**1**, 539.4 mg, 2.37 mmol), whereas a MeCN (10 mL) solution of $[\text{Et}_4\text{N}^+][\text{Cl}^-]$ (844.4 mg, 5.09 mmol, 0.51 M) was placed in the cathodic chamber. These chambers were connected with a tube and duct to take a balance

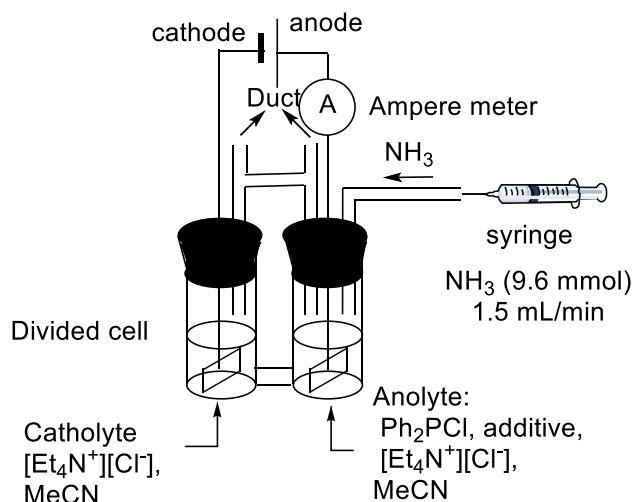


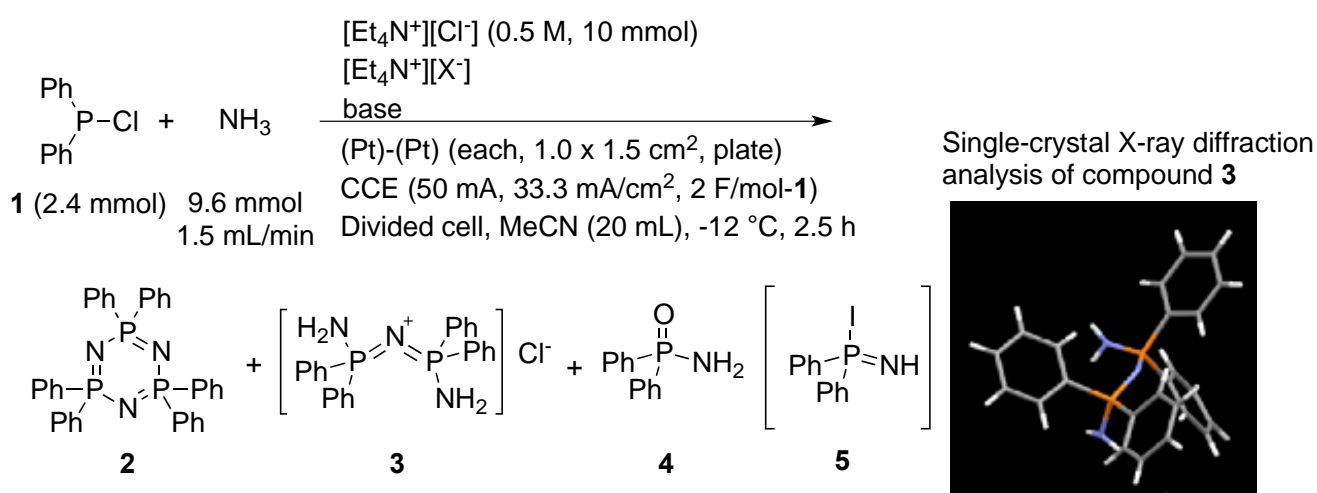
Figure 1. Reactor: Divided Cell

of the pressure of the both chambers. The solutions were electrolyzed under constant current (50 mA, $31 \mu\text{F/min}$, 154 min, 2 F/mol-1) conditions at -12°C with vigorous stirring. During the electrolysis, NH_3 gas was supplied by using a syringe (1.5 mL/min, $62 \mu\text{mol/min}$, 154 min, total: 238 mL, 9.58 mmol assuming that NH_3 is an ideal gas)⁴ to form NH_4Cl gradually. After the electrolysis, the anolyte was filtered to remove NH_4Cl . The filtrate was concentrated in *vacuo*, and the residue was analyzed by ^{31}P NMR to find that a mixture of 2,2,4,4,6,6-hexaphenylcyclotriphosphazene (**2**, 18%), iminobis(aminodiphenylphosphorus) chloride (**3**, 40%), and diphenylaminophosphine oxide (**4**, 28%) was obtained. THF (5 mL) was added to the residue, and the mixture was allowed to stand overnight, and

the precipitated crystals **3** were isolated by filtration. Structure of **3** was confirmed by single-crystal X-ray diffraction analysis.⁵ **2** was purified by silica gel chromatography of the mother liquor of the recrystallization procedure.

Effects of halide ion sources were investigated (Table 1). When tetraethylammonium iodide was added to the electrooxidation system, the yield of **2** was improved up to 30% (Entry 2). On the other hand, addition of tetraethylammonium bromide did not improve the yields of **2** and **3** (Entry 3). This result was similar when no halide salt other than chloride salt was added (Entry 1). Since the oxidation potential of I^- is lower than Cl^- , I^- is electrooxidized to I_2 or I^+ , which acts on Ph_2PCl under ammonia atmosphere to give **5**. It is conceivable that the reactivity of the intermediate is improved because the P-I bond is weak. Therefore, the yields **2** and **3** would be increased.

Table 1. Effect of Halogen Additives and Bases



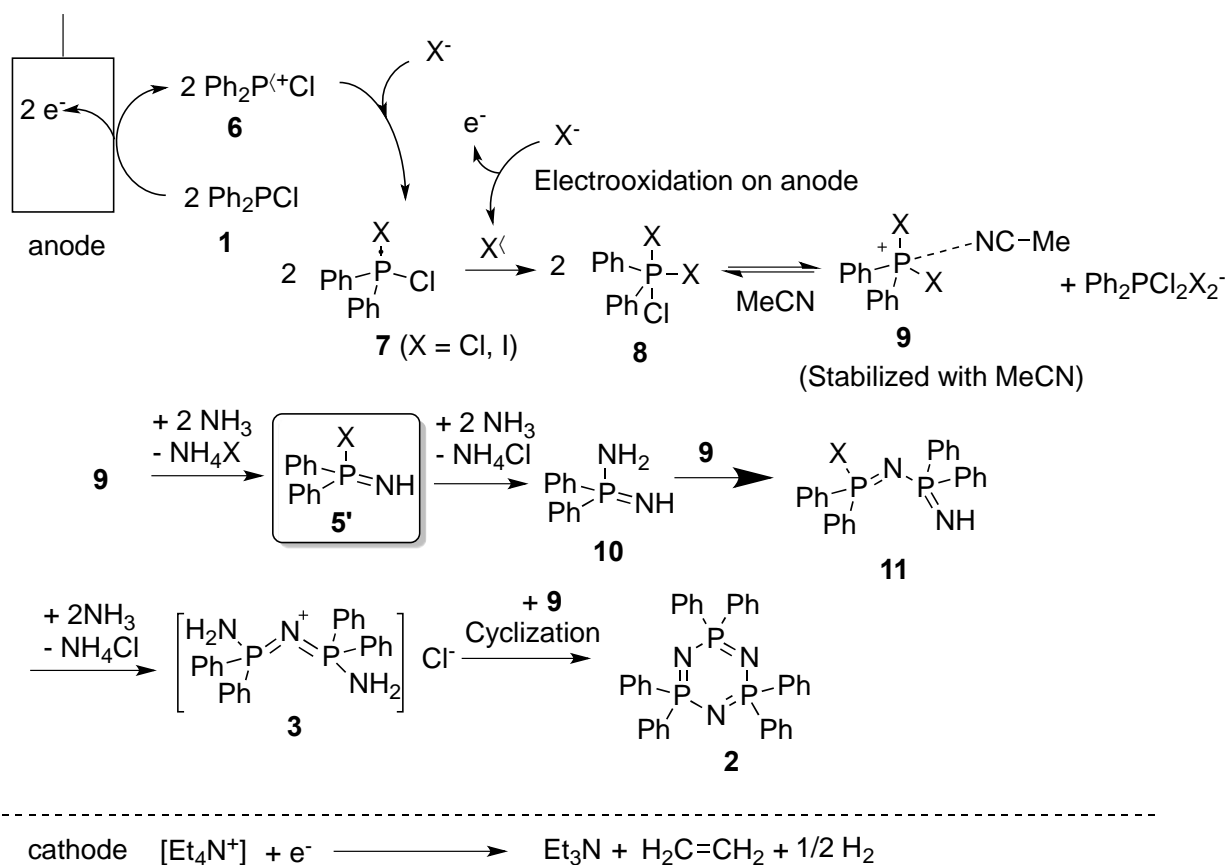
Entry	X	amount /mmol	base	amount /mmol	Ratio/% ^a		
					2	3	4
1	none	0	none	0	18	40	28
2	I	1	none	0	30	35	18
3	Br	1	none	0	16	37	32
4	none	0	Py	5	10	23	15
5	none	0	DMAP	5	13	17	15
6 ^b	none	0	Et ₃ N	5	8	25	trace
7 ^b	none	0	^t Pr ₂ NEt	5	13	41	24

^a ³¹P NMR ratio.

^b Four unidentified products were appeared at 37.6, 36.1, -21.0, -22.4 ppm singlet (each peaks had the same ratio).

When hexachlorocyclotriphosphazene was synthesized from PCl_5 and NH_4Cl , the cyclized product was

A plausible reaction mechanism is as follows (Scheme 3). At first, **1** is electrooxidized on the anode to obtain $\text{Ph}_2\text{P}^+\text{Cl}^-$ (**6**). **6** would react with Cl^- to obtain $\text{Ph}_2\text{P}^+\text{Cl}_2^-$ (**7**). Cl^- is also electrooxidized to obtain Cl^\cdot . **7** would react with Cl^\cdot to afford $\text{Ph}_2\text{P}^+\text{Cl}_3^-$ (**8**). **8** is in equilibrium with $\text{Ph}_2\text{P}^+\text{Cl}_2^-$ (**9**) and $\text{Ph}_2\text{P}^+\text{Cl}_2\text{X}_2^-$ in acetonitrile. **9** would be stabilized with MeCN and react with ammonia to give **5'**. Product selectivity, especially **2** vs. **3**, would depend on supply rate of NH_3 and/or generation rate of **5'**. Though intermediate **9** would be stabilized with MeCN,⁶ the stabilization would not enough at room temperature. When the supply rate of NH_3 was fast, **9** would react with NH_3 smoothly to afford **5'** and **10** (Path I). **10** would react with **9** to give **11**. **11** would further react with NH_3 to give **3**. On the other hand, when the reaction was carried out at $-12\text{ }^\circ\text{C}$, life time of **9** would be elongated to give **3** in moderate yield regardless of current and the supply rate of NH_3 . **2** would be obtained from the reaction of **3**, **9**, and NH_3 . When the electrolysis was carried out at lower temperature and **9** would be generated in a sufficient rate, yield of **2** would increase.



Scheme 3. A Plausible Reaction Mechanism

In conclusion, the electrooxidation of $\text{Ph}_2\text{P}(\text{Ph})\text{Cl}$ (**1**)⁷ under NH_3 atmosphere gave hexaphenylcyclotriphosphazene (**2**) and iminobis(aminodiphenylphosphorus) chloride (**3**). The electrooxidation promote these reactions smoothly under mild reaction conditions. By oxidizing Cl^- and

1, phosphazene compounds can be obtained without using toxic chlorine gas. It is conceivable that $\text{Ph}_2\text{P}(=\text{NH})\text{Cl}$ (**5**) is an intermediate in this reaction. The stability of **5** seems to be a key factor for chemoselective synthesis of the product (**2** vs. **3**). The stability of **5** would depend on supply rate of NH_3 and the rate of **5** generated by electrooxidation.

By adding $[\text{Et}_4\text{N}^+][\text{I}^-]$, yields of **2** and **3** were improved. It is considered that I^- stabilizes the intermediate.

At this point, the reaction conditions for selective generation of **2** and/or **3** are as follows.

- Conditions for **2**: at $-12\text{ }^\circ\text{C}$, 50 mA, NH_3 supplying rate at 1.5 mL/min, **4** was obtained in 30% yield.
- Conditions for **3**: at room temperature, 100 mA, NH_3 supplying rate at 3.1 mL/min, **3** was obtained in 59% yield.

EXPERIMENTAL

Spectral data of 2, 3, and 4. 2,2,4,4,6,6-Hexaphenylcyclotriphosphazene (**2**):¹ ^{31}P NMR (160 MHz, CDCl_3) δ 16.32. Iminobis(aminodiphenylphosphorus) chloride (**3**): ^{31}P NMR (160 MHz, CDCl_3) δ 20.49; ^1H NMR (400 MHz, CDCl_3) δ 5.14 (br, 4H), 7.42-7.47 (m, 8H), 7.51-7.56 (m, 4H), 7.91-7.98 (m, 8H); IR (KBr) 526, 688, 719, 971, 1124, 1252 (br), 1438, 1558, 3060, 3172 cm^{-1} . Diphenylaminophosphine oxide (**4**): ^{31}P NMR (160 MHz, CDCl_3) δ 22.84.

X-Ray crystallographic data of 3: THF (5 mL) was added to the anolyte after the electrooxidation, and the mixture was allowed to stand overnight to form precipitated crystals of **3**. **3** was recrystallized from THF solution. $\text{C}_{24}\text{H}_{24}\text{ClN}_3\text{P}_2$, $M = 451.87$, triclinic, $a = 9.315(4)$, $b = 11.182(5)$, $c = 11.591(6)$ Å, $\alpha = 81.12(2)$, $\beta = 81.60(2)$, $\gamma = 73.355(19)^\circ$, $V = 1136.2(9)$ Å³, calculated density is 1.321 g/cm^3 , $T = 100$ K, space group P_{-1} (no. 2), $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.71075$ Å, 18094 reflections measured, 5186 unique ($R_{\text{int}} = 0.0614$), which were used in all calculations. The final $R_1 = 0.0499$ ($I > 2\sigma(I)$) and $R_w = 0.1227$ (all data).

X-Ray data for **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1935453. Copies of the data may be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

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4. The balance of the feed rate of NH₃ and electricity was important: *i. e.* supply rate of NH₃ (mmol-NH₃/min) was set as twice of electricity (mF/min, supply rate of the oxidant). Otherwise, only a complex mixture of unidentified products was obtained. Though electrooxidation is not familiar for many chemists, it can provide useful reagents and/or intermediates constantly in a desired rate.
5. When aq. NH₃ and NaOCl was used in place of gaseous NH₃ and electrooxidation, Ph₂P(=O)OH (oxidation/hydrolysis product) was obtained as a sole product and neither **2** nor **3** was obtained. When some oxidants such as NBS, NCS, and ICl/Py under gaseous NH₃ atmosphere, only a complex mixture of unidentified products was obtained.
6. R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore, [J. Am. Chem. Soc., 1973, 95, 1474.](#)
7. Ar₂PCl can be prepared by several methods such as 1) reaction of ArPCl₂ with Grignard reagent, 2) ArPCl(NR₂) with Grignard reagent, 3) Friedel-Crafts reaction of ArPCl₂ with ArH in the presence of AlCl₃, 4) Ar₂PNR'₂ and/or Ar₂POH with HCl. Some of them are commercially available.