HETEROCYCLES, Vol. 98, No. 9, 2019 pp. 1258 - 1264. © 2019 The Japan Institute of Heterocyclic Chemistry
Received, 21st August, 2019, Accepted, 18th September, 2019, Published online, 1st October, 2019
DOI: 10.3987/COM-19-14150

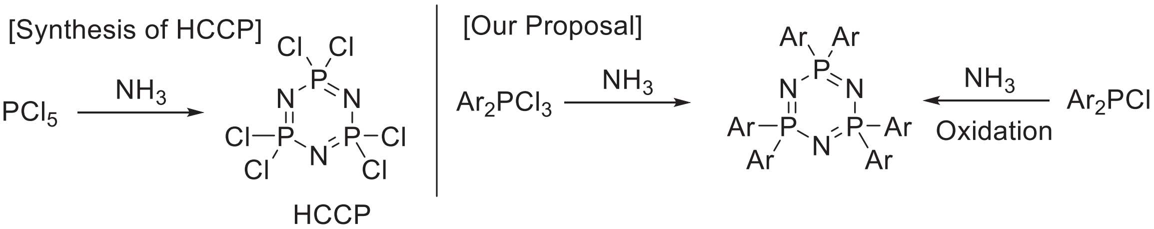
ELECTROOXIDATION OF CHLORODIPHENYLPHOSPHINE UNDER AMMONIA ATMOSPHERE. SYNTHESIS OF 2,2,4,4,6,6-HEXAPHENYLCYCLOTRIPHOSPHAZENE AND IMINOBIS(AMINODIPHENYLPHOSPHORUS) CHLORIDE

Manabu Kuroboshi,* Yasunari Masumoto, and Hideo Tanaka

Graduate School of Natural Science and Technology, Okayama University, Tsushima-naka 3-1-1, Kita-ku, Okayama, Japan. 700-7530, mkurohos@cc.okayama-u.ac.jp

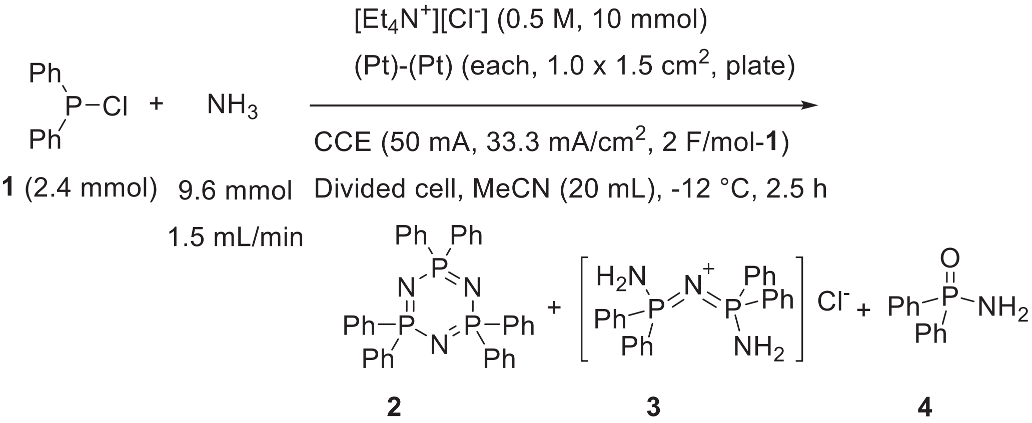
Abstract – Electrooxidation of MeCN solution of chlorodiphenylphosphine in the presence of Cl^- under NH_3 atmosphere gave a mixture of 2,2,4,4,6,6-hexaphenylcyclotriphosphazene and iminobis(aminodiphenylphosphorus) chloride.

Cyclotriphosphazene has a 6-membered heterocyclic ring in which three P atoms and three N atoms are alternately connected. Hexaarylcyclotriphosphazene [$(Ar_2PN)_3$] was investigated as a host materials in blue phosphorescent organic light-emitting diodes.[1] [$(Ar_2PN)_3$] was prepared by 1) reaction of [$(Cl_2PN)_3$] and ArMgBr[2] or 2) reaction of $Ar_2P(=O)NH_2$ and PPh_3/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 [$(Cl_2PN)_3$, HCCP] is industrially synthesized from PCl_5 and NH_4Cl,[3] [$(Ar_2PN)_3$] may be produced from a reaction of Ar_2PCl_3 and NH_3 or Ar_2PCl and NH_3 under oxidation conditions (Scheme 1).



Scheme 1. Preparation of Cyclotriphosphazenes

We investigated electrooxidation of Ph$_2$PCl (**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 [(Ph$_2$PN)$_3$, **2**] and iminobis(aminodiphenylphosphorus) chloride [[(NH$_2$PAr$_2$)$_2$N$^+$]Cl$^-$, **3**] was obtained (Scheme 2).



Scheme 2. Reaction of Ph$_2$PCl and NH$_3$ under electrooxidation conditions

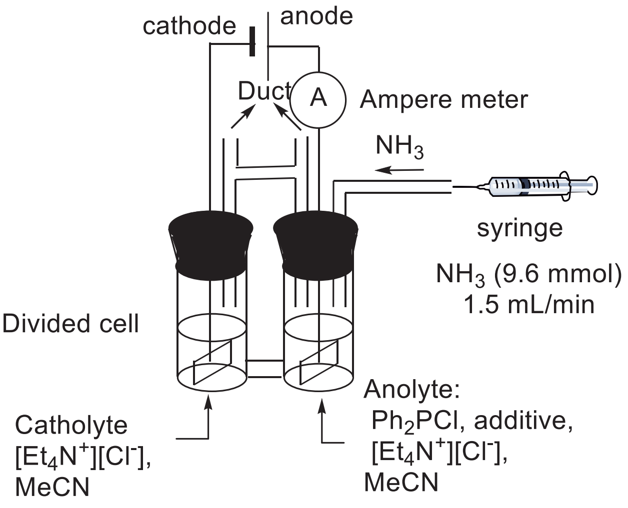
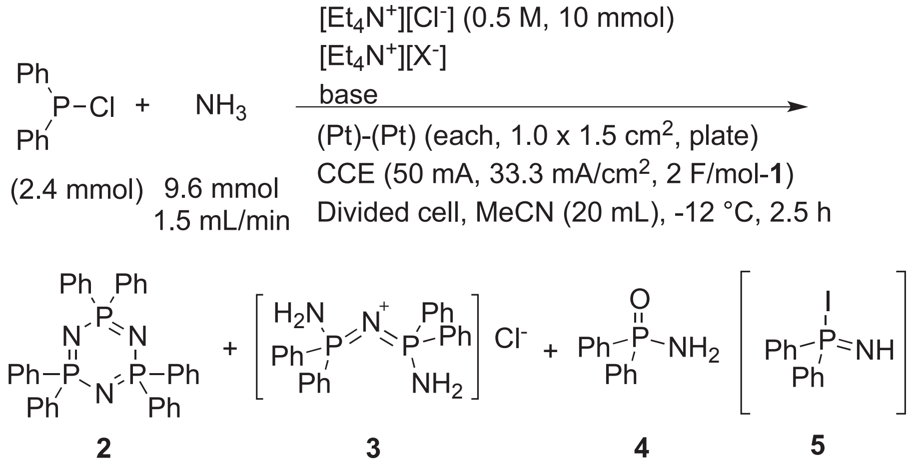


Figure 1. Reactor: Divided Cell

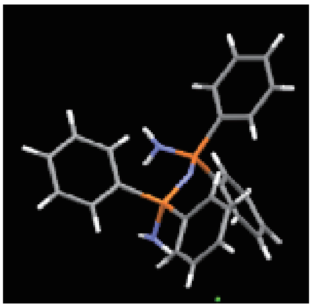
The typical procedure was as follows. The electrolysis was carried out in a divided cell equipped with magnetic stirring bars and Pt electrodes (1.5 x 1.0 cm^2) (Figure 1). In the anodic chamber was placed a MeCN (10 mL) solution of [Et$_4$N$^+$][Cl$^-$] (830.8 mg, 5.01 mmol, 0.51 M) and Ph$_2$PCl (**1**, 539.4 mg, 2.37 mmol), whereas a MeCN (10 mL) solution of [Et$_4$N$^+$][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 of the pressure of the both chambers. The solutions were electrolyzed under constant current (50 mA, 31 μF/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 μmol/min, 154 min, total: 238 mL, 9.58 mmol assuming that NH$_3$ is an ideal gas)[4] to form NH$_4$Cl gradually. After the electrolysis, the anolyte was filtered to remove NH$_4$Cl. 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 electrooxiation 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



Single-crystal X-ray diffraction analysis of compound **3**



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_3N	5	8	25	trace
7[b]	none	0	$^iPr_2NEt$	5	13	41	24

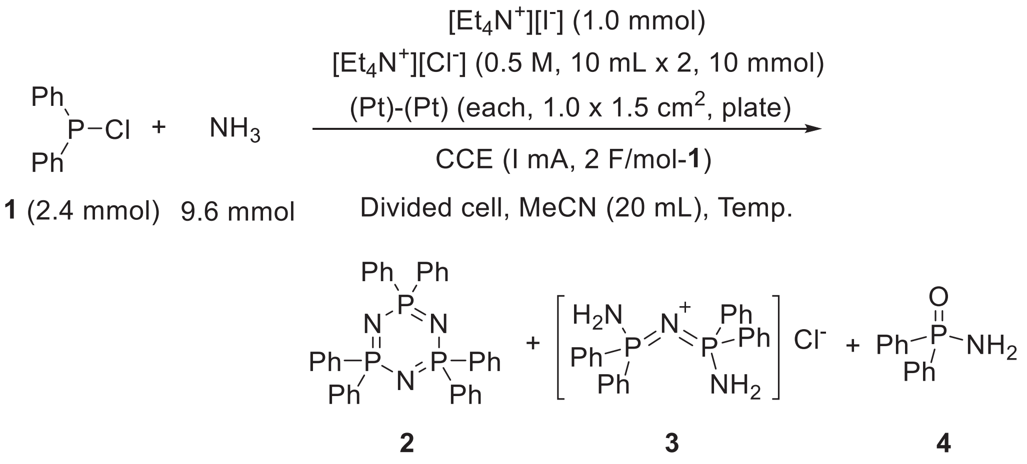
[a] ^{31}P NMR ratio.

[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 preferentially obtained in the presence of tertiary amines as bases. Bases are added to facilitate the cyclization and elimination of hydrogen chloride reaction. Therefore, we also examined the effect of bases (Entries 4-7). Though pyridine (Entry 4), DMAP (Entry 5), trimethylamine (Entry 6), and ethyldiisopropylamine (Entry 7) were used as bases, ^{31}P NMR yields of **2** and **3** decreased in all cases. It seems that the active species, $Ph_2P(=NH)Cl$, would undergo nucleophilic substitution with a base.

Therefore, reaction temperature, feed rate of NH_3, and current were optimized (Table 2). When the reaction was carried out at room temperature, current was 100 mA (64 μF/min), and NH_3 supplying rate at 3.1 mL/min (128 μmol/min), **3** was mainly obtained in 59% yield together with 9% of **2** (Entry 1). Decrease of current and supply rate of NH_3 caused decrease of yield of **3**, and neither **2** nor **3** was obtained at current 25 mA (16 mF/min) and supply rate of NH_3 was 0.8 mL/min (32 μmol/min) (Entry 3). On the other hand, when the electrolysis was carried out at lower temperature, -12 ºC, **3** was obtained in 31-42% yield (Entries 4-6), and when the current was 50 mA (32 mF/mol) and the supply rate of NH_3 was 1.5 mL/min (64 μmol/min), the yield of **2** increased up to 30% (Entry 5).

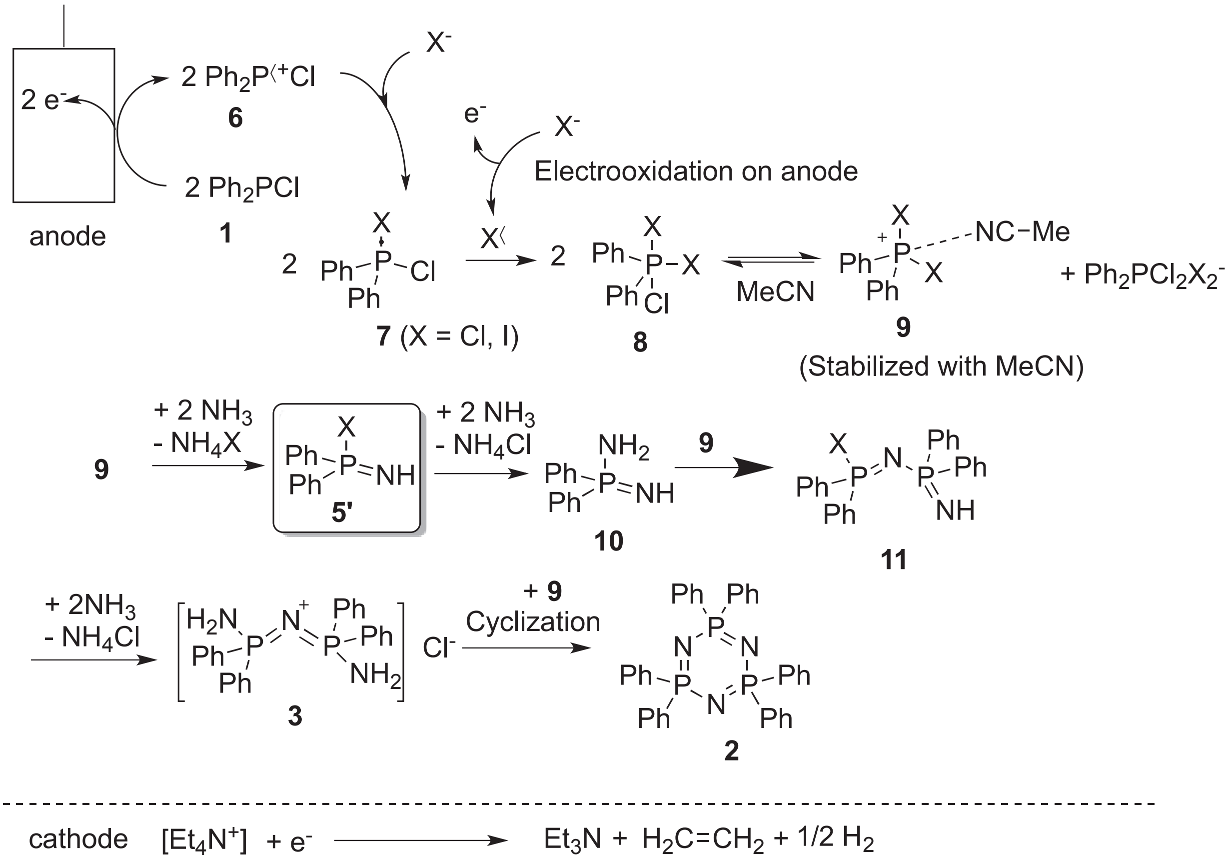
Table 2. Reaction Temperature, Feed Rate of NH_3, and Currents



Entry	Temp.	mA	μF/min	NH_3 (mL/min)	mmol[a]/min	Time (min)	Yield[b] (%) 2	3	4
1	rt	100	64	3.1	128	77	9	59 (50)[c]	8
2	rt	50	32	1.5	64	154	13	38	14
3	rt	25	16	0.8	32	308	N.D.[d]	N.D.[d]	N.D.[d]
4	-12 ºC	75	48	2.0	96	77	11	31	21
5	-12 ºC	50	32	1.5	64	154	30	35	18
6	-12 ºC	25	16	0.8	32	308	14	42	N.D.

[a] Supply rate of NH_3 (mmol-NH_3/min) was set as twice of electricity (μF/min).
[b] Determined by ^{31}P NMR ratio. [c] Isolated yield. [d] Not detected.

A plausible reaction mechanism is as follows (Scheme 3). At first, **1** is electrooxidized on the anode to obtain $Ph_2PCl^{\cdot +}$ (**6**). **6** would react with Cl^- to obtain $Ph_2PCl_2^{\cdot}$ (**7**). Cl^- is also electrooxidized to obtain $Cl^{\cdot}$. **7** would react with $Cl^{\cdot}$ to afford Ph_2PCl_3 (**8**). **8** is in equilibrium with $Ph_2PCl_2^+$ (**9**) and $Ph_2PCl_2X_2^-$ 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 ºC, 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 Ph_2PCl (**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 $Ph_2P(=NH)Cl$ (**5**) is an intermediate in this reaction. The stability of **5** seems to be a key factor for chemoselective synthesys 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 $[Et_4N^+][I^-]$, 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 followes.

- Conditions for **2**: at -12 ºC, 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; **^{1}H 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. $C_{24}H_{24}ClN_3P_2$, M = 451.87, triclinic, a = 9.315(4), b = 11.182(5), c = 11.591(6) Å, α = 81.12(2), β = 81.60(2), γ = 73.355(19)º, V = 1136.2(9) Å^3, calculated density is 1.321 g/cm^3, T = 100 K, space group P_{-1} (no. 2), Z = 2, μ(Mo-Kα) = 0.71075 Å, 18094 reflections measured, 5186 unique (Rint = 0.0614), which were used in all calculations. The final R1 = 0.0499 (I > 2σ(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).

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Prof. Hiromi Ota, Okayama University Advanced Science Research Center, for X-ray crystal analysis.

REFERENCES AND NOTES

1. P. Schrögel, M. Hoping, W. Kowalsky, A. Hunze, G. Wagenblast, C. Lennartz, and P. Strohriegl,

Chem. Mater., 2011, **23**, 4947.

2. F. Aslan and M. Arslan, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2008, **183**, 2875.
3. J. Liebig and J. Wöhler, *Justus Liebigs Ann. Chem.*, 1934, **11**, 146; H. N. Stoke, *Am. Chem. J.*, 1895, **17**, 275.
4. The balance of the feed rate of NH_3 and electricity was important: *i. e.* supply rate of NH_3 (mmol-NH_3/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. NH_3 and NaOCl was used in place of gaseous NH_3 and electrooxidation, $Ph_2P(=O)OH$ (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 NH_3 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. Ar_2PCl can be prepared by several methods such as 1) reaction of $ArPCl_2$ with Grignard reagent, 2) $ArPCl(NR_2)$ with Grignard reagent, 3) Friedel-Crafts reaction of $ArPCl_2$ with ArH in the presence of $AlCl_3$, 4) $Ar_2PNR'_2$ and/or Ar_2POH with HCl. Some of them are commercially available.