



AlCl₃-catalyzed C-H p hosphination of benzene: A mechanistic study

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ABSTRACT

The characteristics of the reaction for the preparation of dichlorophenylphosphine (DCPP) via benzene and PCl₃ in the presence of AlCl₃ were studied. Some unique characteristics were observed when a catalytic amount of AlCl₃ was used. Namely, more than one mole of DCPP was obtained per mole AlCl₃, the reaction solution was layered, and DCPP could be directly separated. Our mechanistic study showed that benzene reacted with PCl₃ to form DCPP-AlCl₃, and DCPP-AlCl₃ dissociated into DCPP and AlCl₃, continuing to catalyze this reaction. This resulted in the high catalytic efficiency of AlCl₃. The layering of the reaction solution was caused by the immiscibility of DCPP-AlCl₃ with the raw materials, greatly facilitating the dissociation process of DCPP-AlCl₃. The formation of diphenylphosphorus chloride (DPC) was due to a continuous Friedel-Crafts reaction between DCPP and benzene. DPC cooperated with AlCl₃ to form the stable coordination compound DPC-AlCl₃ that did not dissociate and was responsible for the deactivation of AlCl₃.

1. Introduction

Dichlorophenylphosphine (DCPP) is an important organophosphorus compound that is widely used in the preparation of flame retardants, photoinitiators, insecticides, plasticizers, and stabilizers [1]. According to previous reports, DCPP has been obtained by the following synthetic methods: (i) free radical reaction of chlorobenzene, PCl₃, and elemental phosphorus in the presence of AlCl₃ [2], (ii) Friedel-Crafts reaction of benzene and PCl₃ promoted by AlCl₃ [3], (iii) Grignard reaction of chlorobenzene and PCl₃ [4], and (iv) transformation of the derivatives of DCPP via reduction, chlorination, or pyrolysis reaction [5]. Of these four methods, the first two have been used in the industrial production of DCPP. However, the first method is limited due to its harsh reaction conditions and difficulty of product purification, while the second method requires the use of stoichiometric or much greater loadings of AlCl₃, resulting in the coordination of AlCl₃ and the DCPP product, which is similar to Friedel-Crafts acylation [6]. This requires the subsequent use of a decomplexation process to separate DCPP from AlCl₃ (Scheme 1, equation 1a). To obtain DCPP, various reagents such as phosphorus oxychloride, pyridine, sodium chloride, potassium chloride, phosphonic acid, and water have been used to disrupt the coordination

of DCPP and AlCl₃ [3a-3f]. Although DCPP was successfully isolated using these decomplexation reagents, this approach generated a large quantity of solid waste. While Neumaier reported that significantly more than one-mole DCPP per mole AlCl₃ was obtained when 0.05–0.9 moles AlCl₃ per mole benzene was used in DCPP synthesis, the decomplexation process was still necessary and no further studies were performed pursuing this research direction [7].

In 2003, Wang and co-workers first reported on the use of ionic liquids in the preparation of DCPP via Friedel-Crafts reaction (Scheme 1b) [8] and since then, this approach has been explored in several studies [9]. The reaction conducted in the presence of ionic liquids shows advantages such as low dosage of catalyst and simple product isolation. Although the amount of solid waste was greatly decreased when the reaction was catalyzed by ionic liquids, the addition of quaternary ammonium salts made the solid waste more difficult to handle [10]. Thus, the development of novel methods for the preparation of DCPP and detailed study of the reaction mechanism of DCPP synthesis are still highly important.

In the present work, it was found that when a catalytic amount of AlCl₃ was used in the synthesis of DCPP via Friedel-Crafts reaction, the reaction was similar to that catalyzed by ionic liquids (Scheme 1c).

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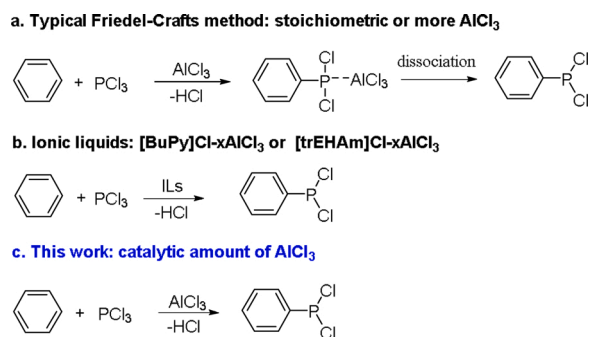
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Scheme 1. Synthetic methods of DCPP via Friedel-Crafts reaction.

Notably, a layered solution was obtained after the reaction, and DCPP could be easily isolated. Moreover, the yield of DCPP was significantly higher than the amount of the AlCl₃ used. Then, the reaction of benzene and PCl₃ in the presence of the catalytic amount of AlCl₃ was studied and the reaction mechanism was elucidated.

2. Results and discussion

2.1. Discovery of reaction characteristics

In the preparation of DCPP via the reaction of benzene and PCl₃, a homogeneous solution was obtained when a stoichiometric amount of AlCl₃ was used (Fig. 1a). In this case, the product could not be separated directly (Table 1, entry 1). When the dosage of AlCl₃ was reduced to 10 % of benzene, the reaction solution was divided into a colorless layer and a yellow layer (Fig. 1b). After distillation, the unreacted benzene and PCl₃ were recovered from the colorless layer and DCPP was obtained (Fig. S1). The follow-up quantitative experiments showed that the amount of DCPP obtained in the colorless layer was 2.11 times greater than that of the AlCl₃ used (Table 1, entry 2). These results indicated that when a catalytic amount of AlCl₃ was used in the reaction of benzene and PCl₃, AlCl₃ acted as the catalyst. Very little residue was obtained after the distillation of the colorless layer, indicating that the layer contained almost no AlCl₃. This suggested that the main component of the yellow layer was AlCl₃ and the substance coordinated with it. The yellow layer which was also called the catalyst layer was analyzed as described below.

The effects of the dosage of catalyst, the PCl₃-to-benzene ratio, reaction time, and reaction temperature on the catalytic efficiency of AlCl₃ (defined as the amount of product obtained per mole AlCl₃) were investigated, with the results shown in Table 1. It was found that the catalytic efficiency of AlCl₃ was significantly improved by reducing the dosage of AlCl₃ when the PCl₃-to-benzene ratio was 1.9:1 (Table 1,

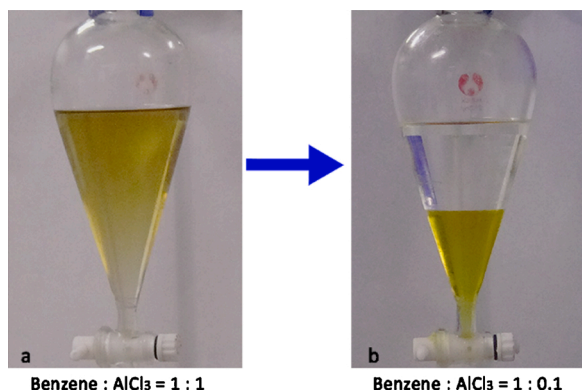


Fig. 1. Reaction solutions of benzene and PCl₃ in the presence of AlCl₃. Reaction conditions: benzene (0.1 mol), PCl₃ (0.19 mol), 80 °C, 8 h.

Table 1
Reaction Optimization^a.

Entry	PCl ₃ (equiv.)	AlCl ₃ (mol%)	t (h)	Catalytic efficiency ^b
1	1.9	100	8	0
2	1.9	10	8	2.11
3	1.9	7	8	2.99
4	1.9	5	8	3.37
5	1.9	3	8	4.89
6	1.9	2	8	4.85
7	1.5	3	8	4.44
8	2.2	3	8	5.43
9	2.5	3	8	5.26
10	1.9	3	4	3.96
11	1.9	3	6	4.88

^a Reaction conditions: benzene (0.1 mol), PCl₃ (1.9–2.5 equiv.), AlCl₃ (2–100 mol%), 80 °C, 4–8 h.

^b Catalytic efficiency of AlCl₃: DCPP was determined by GC using *n*-hexadecane as an internal standard.

entries 1–6) and 4.89 mol DCPP were obtained per mole AlCl₃ when the AlCl₃ dosage was reduced to 3% of benzene (Table 1, entry 5). The catalytic efficiency of AlCl₃ was no longer significantly improved when the dosage of AlCl₃ was further reduced. The catalytic efficiency of AlCl₃ increased with increasing PCl₃ dosage (vs. benzene) when the AlCl₃ content was 3% (Table 1, entries 5, and 7–9). When the PCl₃-to-benzene ratio increased to 2.2:1, 5.43 mol DCPP were obtained per mole AlCl₃ (Table 1, entry 8). Investigation of the reaction time showed that the catalytic efficiency of AlCl₃ increased slowly with reaction time for the reaction times greater than 6 h at 80 °C (Table 1, entries 5, 10, and 11). Examination of the effects of the reaction temperature showed that increasing the reaction temperature improved the catalytic efficiency of AlCl₃ (Fig. 2).

2.2. Scale-up experiment

To verify the feasibility of this method for industrial production of DCPP, a scale-up experiment was carried out under the optimized conditions and compared with typical Friedel-Crafts method, with the results summarized in Table 2. It was found that despite a slight increase in the consumption of benzene due to the recovery loss with our method, the catalytic efficiency of AlCl₃ was 6.56 times greater than that of the typical Friedel-Crafts method, and the decomplexation process was avoided. Moreover, the generation of solid waste was reduced by 90 %. Thus, the new method offers reliable and scalable access to the preparation of DCPP.

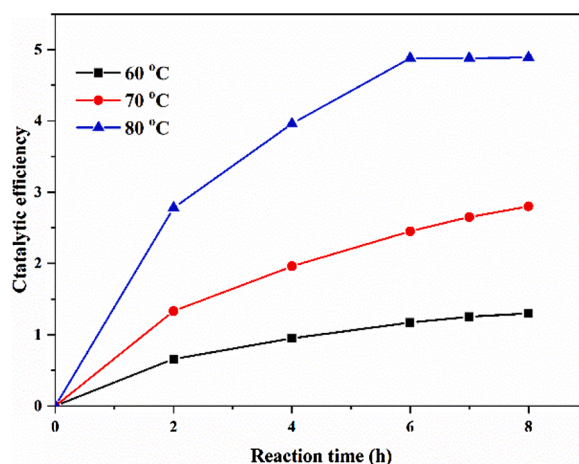


Fig. 2. Influence of reaction temperature on the catalytic efficiency of AlCl₃.

Table 2

Comparison of raw materials consumption and solid waste generation between typical Friedel-Crafts method and our method when preparing 1 mol DCPP^a.

Entry	Benzene (mol)	AlCl ₃ (mol)	Et ₃ N·HCl (mol)	Solid waste (g)
1 ^b	1.23	1.18	1.18	344
2 ^c	1.30	0.18	–	36

^a Reaction conditions : benzene (1 mol), PCl₃ (1.9 equiv.), AlCl₃, 80 °C, 6 h.

^b Typical Friedel-Crafts method: Et₃N·HCl (1 mol) was used as the decomplexation reagent.

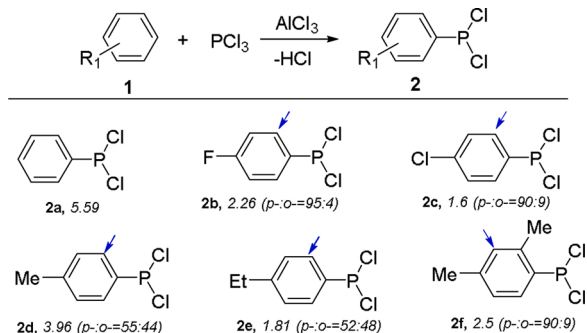
^c Our method: recovery of benzene (0.79 mol, 94.2 %), the yield of DCPP (77 %).

2.3. Substrate scope

Based on these promising results, the universality and limitations of the reaction between arenes and PCl₃ were explored with the results summarized in Scheme 2. It was found that more than one mole of products was obtained per mole AlCl₃ for all substrates when the catalytic amount of AlCl₃ was used in this reaction. However, for other substrates, both with electron-withdrawing (-F, -Cl) and electron-donating groups (-Me, -Et), the catalytic efficiency of AlCl₃ was far lower than that in the preparation of 2a. The decrease in the AlCl₃ catalytic efficiency was attributed to the low reactivity of the arene caused by the electron-withdrawing groups (Scheme 2, b, and c). While electron-donating groups endowed the arene with higher reactivity, the formation of a more stable coordination compound between the product and AlCl₃ also resulted in the low catalytic ability of AlCl₃, as demonstrated by the decrease in the catalytic efficiency of AlCl₃ with increasing number of electron-donating groups (Scheme 2, a, d, and f). N-methylpyrrole also gave the target product as shown in Fig. S2.

2.4. Mechanistic study

Based on the above results and previous reports on the reaction of benzene and PCl₃ in the presence of AlCl₃, the reaction mechanism in the presence of a catalytic amount of AlCl₃ was studied in detail. It is reasonable to suppose that AlCl₃ coordinates with PCl₃, DCP, and DPC, in two configurations, namely either through the coordination of the Al atom with the P atom (Fig. 3, Type I) or through the coordination of the Al atom with the Cl atom (Fig. 3, Type II). Analysis of the electrostatic potential on the molecular surface can be used to predict the coordination points between the two molecules, and was used to verify the proposed coordination modes [11]. It was found that the local electrostatic potential in PCl₃, DCP, and DPC had two local minima. The first minimum ($V_{s, \text{min}, \text{p}}$) was located directly above the P atom, corresponding to the lone pair electrons of the P atom. The second minimum ($V_{s, \text{min}, \text{Cl}}$) corresponded to the negative electrostatic potential around the Cl atom [12]. Additionally, a local maximum of the electrostatic



Scheme 2. Substrate scope^{a,b}.

^a Reaction conditions: arene (1 mol), PCl₃ (1.9 mol) and AlCl₃ (0.03 mol), 80 °C, 6 h.

^b Catalytic efficiency of AlCl₃.

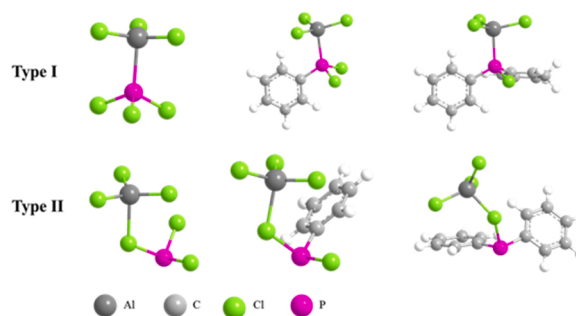


Fig. 3. Proposed coordination forms of AlCl₃ with PCl₃, DCP, and DPC.

potential was found above the Al atom in AlCl₃ (61.85 kcal mol⁻¹). Therefore, for each of the three molecules (PCl₃, DCP, and DPC), the Al atom attacked the region with a minimum value of the electrostatic potential to form a coordination compound due to the electrostatic attraction. As shown in Table 3, the $V_{s, \text{min}, \text{p}}$ and $V_{s, \text{min}, \text{Cl}}$ values in DCP and DPC were both negative, so that two types of coordination compounds can be formed. This validated the proposed coordination mode. The two configurations were also confirmed by the ³¹P NMR of DCP-AlCl₃ and DPC-AlCl₃ (Fig. S3). The presence of three strong electron-withdrawing chlorine atoms gave rise to the positive value of $V_{s, \text{min}, \text{p}}$ in PCl₃. Therefore, PCl₃ only coordinated with AlCl₃ in the Type II configuration. It was also found that both $V_{s, \text{min}, \text{p}}$ and $V_{s, \text{min}, \text{Cl}}$ decreased greatly when the Cl atoms in PCl₃ were replaced by benzene rings. This indicated that the coordination ability of AlCl₃ with the three molecules was in the order of DPC > DCP > PCl₃.

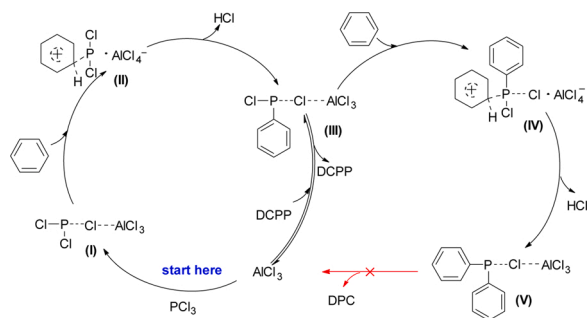
Based on the above coordination modes, the mechanism of the reaction of benzene and PCl₃ catalyzed by the catalytic amount of AlCl₃ was proposed. Since PCl₃ only coordinated with AlCl₃ in the Type II configuration, PCl₃ was endowed with electrophilic ability due to the effect of AlCl₃ (Scheme 3, I). Then, the generated electrophilic species underwent an electrophilic substitution reaction with benzene to form DCP-AlCl₃ (Scheme 3, III). Different from the common view that DCP forms a stable compound with AlCl₃ leading to the deactivation of AlCl₃, our results indicate that DCP and AlCl₃ maintain a coordination/dissociation equilibrium in the catalyst layer. More importantly, the immiscibility of DCP-AlCl₃ with the raw materials greatly promoted the dissociation process. The Friedel-Crafts reaction still proceeded due to the continuous AlCl₃ dissociation from DCP-AlCl₃. DCP was obtained when DCP-AlCl₃ was extracted by PCl₃, proving the existence of the dissociation process (Fig. S4).

The proposed mechanism for the reaction of benzene and PCl₃ in the presence of AlCl₃ implies that AlCl₃ can be recycled. However, it was found that the catalytic efficiency decreased significantly in the subsequent three runs when the catalyst layer was recycled directly (Table 4, entries 1–3). The obtained catalyst layer was not as transparent as DCP-AlCl₃ and its appearance was similar to that of DPC-AlCl₃ (Fig. S5). This suggested that DPC was generated in the reaction of benzene and PCl₃ under the action of AlCl₃. Then, DPC was obtained by the addition of triethylamine hydrochloride into the catalyst layer, confirming our hypothesis (Fig. S6). Additionally, the fact that DPC was only obtained in the catalyst layer indicated that DPC formed a stable coordination compound with AlCl₃ that was insoluble in the raw materials. Therefore, this suggested that the generation of DPC rather than DCP led to the deactivation of AlCl₃.

Table 3

Local minimum values of electrostatic potential in PCl₃, DCP, and DPC.

Entry	Monomer	$V_{s, \text{min}, \text{Cl}}$ (kcal·mol ⁻¹)	$V_{s, \text{min}, \text{p}}$ (kcal·mol ⁻¹)
1	PCl ₃	-5.642	6.775
2	DCP	-15.326	-8.376
3	DPC	-21.645	-18.629



Scheme 3. Plausible mechanism for the preparation of DCP and deactivation of AlCl_3 .

Table 4

Reactions between benzene and PCl_3 catalyzed by the catalyst layer, DCP- AlCl_3 , and DPC- AlCl_3 ^a.

Entry	Catalyst	Catalytic efficiency ^d
1	AlCl_3 ^b	4.89
2	first cycle	0.87
3	second cycle	0.23
4	DCP- AlCl_3 ^c	3.41
5	DPC- AlCl_3 ^c	N.D.

^a Reaction conditions: benzene (0.1 mol), PCl_3 (0.19 mol), catalyst, 80 °C, 6 h.

^b 0.003 mol AlCl_3 .

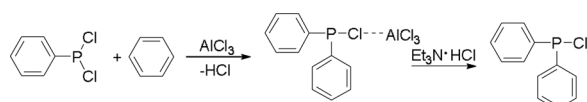
^c Catalyst preparation: DCP or DPC (0.003 mol), AlCl_3 (0.003 mol), 50 °C, 2 h.

^d Catalytic efficiency of AlCl_3 : DCP was determined by GC using n-hexadecane as an internal standard.

To verify this hypothesis, DCP- AlCl_3 and DPC- AlCl_3 were used as the catalysts for the preparation of DCP. It was found that although the catalytic efficiency of DCP- AlCl_3 was lower than that of AlCl_3 , a considerable amount of DCP was obtained when DCP- AlCl_3 was used as the catalyst (Table 4, entry 4). No DCP was detected when the reaction was catalyzed by DPC- AlCl_3 (Table 4, entry 5), indicating that AlCl_3 lost its activity after cooperating with DPC. It was also found that no DCP was detected when DPC- AlCl_3 was extracted with PCl_3 (Fig. S4). This provided additional strong evidence that AlCl_3 formed a stable coordination compound with DPC.

The route for the generation of DPC in this reaction was also studied. Based on the previous reports on the preparation of DPC as well as the possible reactions in the system, DPC can be generated in the following two pathways. The first route is known as DCP disproportionation in the literature [13]. The second route is the Friedel-Crafts reaction between DCP and benzene and has not been reported previously (Scheme 4). Based on the results presented in Table 5, it was concluded that only a small amount of DCP underwent disproportionation, and under mild conditions, DPC was mainly generated through the second pathway.

Based on the above results, the mechanism of the AlCl_3 inactivation during the preparation of DCP by Friedel-Crafts reaction was proposed. AlCl_3 lost its catalytic activity when Type I coordination between AlCl_3 and DCP occurred. This was consistent with the finding that DCP- AlCl_3 had a lower catalytic efficiency than AlCl_3 . When Type II coordination occurred, DCP was endowed with electrophilic ability due to the effect of AlCl_3 (Scheme 3, III) and the generated electrophilic species then underwent an electrophilic substitution reaction with benzene to form DPC- AlCl_3 (Scheme 3, V). Since DPC- AlCl_3 was a stable compound



Scheme 4. Synthetic route of DPC in this system.

Table 5

Preparation of DCP by route 1 and 2.

Entry	Conditions	Yield ^a
1	DCPP (0.1 mol), AlCl_3 (0.1 mol), 80 °C, 6 h.	3
2	DCPP (0.1 mol), AlCl_3 (0.1 mol), benzene (0.1 mol), 80 °C, 6 h.	79

^a Isolated yield.

and did not dissociate, AlCl_3 was inactivated.

2.5. Preparation of DPC and its derivatives via Friedel-Crafts reaction

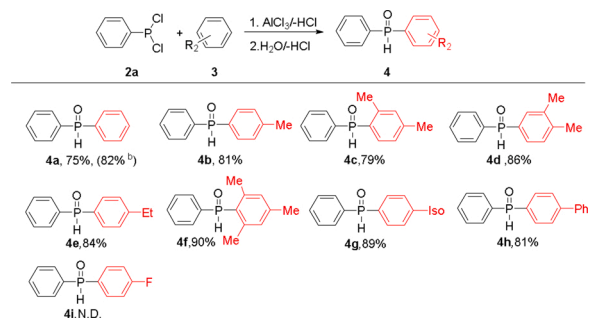
Based on our investigation of the mechanism of catalyst inactivation, it was found that the generation of DPC in the preparation of DCP was due to the Friedel-Crafts reaction between DCP and benzene. Therefore, the feasibility of preparing DPC and its derivatives by this method was explored. In the initial work, the reaction between DCP and benzene was taken as an example. It was found that DPC was obtained in high yields under the optimized conditions (Scheme S1). When the scope of the reaction of DCP and arenes was surveyed, it was found that many diarylphosphorus chlorides with electron-donating groups were difficult to isolate due to their low thermal stability. Diarylphosphine oxides are valuable compounds that have been widely used in the preparation of flame retardants and photoinitiators [14]. For instance, diphenylphosphine oxide (DPO) that is mainly prepared by the hydrolysis of DPC (the disproportionation product of DCP) is an efficient flame retardant for epoxy resin [15]. Therefore, the feasibility of preparing diarylphosphorus oxides through the hydrolysis of the reaction mixture of DCP and arenes was investigated (Scheme 5) using DPO as an example.

To our delight, the desired DPO product was obtained in good yield (Schemes 5, 4Scheme 5a). A scale-up experiment based on the new method was carried out under the optimized conditions, and as shown in Scheme 5, a good yield of 82 % was obtained. Thus, this method provides reliable and scalable access to DPO.

Next, the scope and limitations of the reaction of DCP and arenes were investigated under the optimized conditions, with the results summarized in Scheme 5. It was found that DCP reacted with arenes with electron-donating groups to prepare diarylphosphorus oxides in moderate to good yields in the presence of AlCl_3 . The yield of the products increased with the increasing activity of arene (Schemes 5, 4Scheme 5a, b, d, and f). The steric hindrance of arenes also affected the yield of the products (Schemes 5, 4Scheme 5c, and d). It was found that DCP could not react with the arenes with strong electron-withdrawing groups due to the low reactivity of such arenes (Scheme 5, 4i).

3. Conclusions

In summary, in this work we developed a method for the preparation



Scheme 5. Substrate scope^a.

^a Reaction conditions: DCP (0.05 mol), arene (0.07 mol), AlCl_3 (0.065 mol), 70 °C, 12 h.

^b A scale-up experiment: DCP (0.5 mol), benzene (0.7 mol), AlCl_3 (0.65 mol), 70 °C, 12 h.

of DCPD via Friedel-Crafts reaction from benzene and PCl_3 . The advantages of this method are the reduction of catalyst usage, generation of solid waste, and simple product isolation. Investigation of the reaction mechanism showed that the dissociation of the DCPD- AlCl_3 in the reaction system was responsible for the catalytic properties of AlCl_3 . DCPD reacts with benzene in the presence of AlCl_3 to generate DPC, leading to the deactivation of AlCl_3 . This not only indicates the direction of future research for avoiding catalyst deactivation in the preparation of DCPD but also provides a method for the preparation of diarylphosphine oxides under mild conditions. The synthesis of flame retardants and photoinitiators based on these novel diarylphosphine oxides is currently under investigation in our research laboratory.

4. Experimental section

4.1. General information

Unless otherwise noted, all air and moisture sensitive manipulations were carried out in a nitrogen atmosphere, and all glassware was dried in an oven before use. AlCl_3 , triethylamine hydrochloride, and PCl_3 were industrial products from Jiangsu Fopia Chemicals Co., Ltd. Arenes and n-hexadecane were purchased from Aladdin Industrial Corporation (>99.5 %, GC). DCPD was homemade (>98 %, GC). All reagents were used as received without purification.

4.2. Instrumentation

GC analysis was recorded on a SHIMADZU QP-2014 instrument. Column chromatography was performed using 200–300 mesh silica gels. HPLC analysis was performed on a SHIMADZU LC-20AT instrument. ^1H , ^{13}C , and ^{31}P nuclear magnetic resonance (NMR) spectra of diarylphosphine oxides were obtained on a Bruker Avance III HD spectrometer (500 MHz; Bruker BioSpin GmbH., Rheinstetten, Germany) at room temperature using CDCl_3 as the solvent. Mass data were performed on a Micromass Q-TOF micro instrument.

4.3. General procedure for preparing aryl-phosphorus dichlorides

Under nitrogen atmosphere, in a 500 mL three-necked flask equipped with a magnetic stirrer, thermometer and condenser, arene (1 mol), PCl_3 (1.9 mol) and AlCl_3 (0.03 mol) were added and heated in an oil bath to 80 °C for 6 h. Then, the mixture was cooled to room temperature and transferred to a separatory funnel for liquid separation. The colorless layer, consisting mostly of PCl_3 and arene were removed by distillation at atmospheric pressure, followed by distillation at a slightly reduced pressure below 90 °C. The product was distilled under a high vacuum.

4.4. General procedure for the post-treatment of the catalyst layer

In a 250 mL three-necked flask equipped with a magnetic stirrer, thermometer, triethylamine hydrochloride (6.4 g) was added in portions to the catalyst layer obtained in the scale-up experiment of DCPD synthesis under nitrogen atmosphere. The reaction solution was heated to 70 °C and stirred for 1 h. After PCl_3 (100 g) was added, the mixture was cooled to room temperature and transferred to a separatory funnel for liquid separation. The extraction layer was distilled at atmospheric pressure, followed by distillation at a slightly reduced pressure below 90 °C. The product was distilled under a high vacuum.

4.5. General procedure for preparing diarylphosphine oxides

Under nitrogen atmosphere, in a 50 mL three-necked flask equipped with a magnetic stirrer, thermometer, and condenser, DCPD (0.05 mol), arene (0.07 mol), and AlCl_3 (0.065 mol) were added and heated in an oil bath to 70 °C for 12 h. Then, the mixture was cooled to room temperature and dropped into ice water. After stirring for 1 h, the reaction

mixture was extracted with dichloromethane. The organic phase was washed with aqueous sodium carbonate solution and dried over Na_2SO_4 . The solvent was removed under reduced pressure and a part of the crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to obtain the pure product.

Declaration of Competing Interest

The authors report no declarations of interest.

CRediT authorship contribution statement

Haodong Duan: Conceptualization, Methodology, Writing - original draft. **Xiaolei Xu:** Investigation, Validation. **Kangwei Leng:** Validation. **Ge Guo:** Software. **Qing Yu:** Visualization. **Xinjin Li:** Formal analysis. **Yuxi Han:** Writing - review & editing. **Jun Gao:** Supervision. **Zhongwei Wang:** Resources, Project administration.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcata.2020.117943>.

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