

Computational and ^{31}P NMR studies of moisture-metastable cyclic diaminophosphine oxide preligands



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ABSTRACT

Recently, cyclic heteroatom-substituted secondary phosphine oxides (cyclic HASPOs: $(\text{X}^{\wedge}\text{X})\text{PH}(=\text{O})$, $\text{X} = \text{NR}$ or O atom) have been applied to various catalytic reactions as preligands and with notable success. Similar to secondary phosphine oxides (SPOs: $\text{R}_2\text{PH}(=\text{O})$), cyclic HASPOs are conventionally regarded as air- and moisture-stable compounds. Nevertheless, as reported herein, cyclic diaminophosphine oxides (cyclic N–P–N type HASPO: $(\text{RN}^{\wedge}\text{NR})\text{PH}(=\text{O})$, where $(\text{RN}^{\wedge}\text{NR})$ represents 1,2-diamino group) are susceptible to hydrolysis. The hydrolysis process of two P–N bonds in cyclic diaminophosphine oxides, **1a** and **1b**, has been thoroughly investigated by ^{31}P NMR experiments. Density functional theory (DFT) methods have also been employed for elucidating the reaction mechanisms of hydrolysis for diaminophosphine oxides, **1c** and **1b**, respectively. The results pointed to a stepwise-concerted ($\text{S}_{\text{N}}2\text{I@P4}-\text{S}_{\text{N}}2\text{@P4}$) mechanism for consecutively double hydrolysis of **1c**. **1c** has been employed as a model for **1a** and other diaminophosphine oxides with smaller substituents on nitrogen atoms. In contrast, a concerted-stepwise ($\text{S}_{\text{N}}2\text{@P4}-\text{S}_{\text{N}}2\text{I@P4}$) mechanism for **1b**, bearing two bulky $-\text{tBu}$ groups, was validated. Accordingly, kinetic stability which brought about by two bulky substituents indeed prevents **1b** from being hydrolyzed. The results from ^{31}P NMR experiments also showed that hydrolysis of **1a** proceeded faster in acidic solution than in neutral condition. Unexpectedly, **1a** exhibited unusual resistance toward hydrolysis in alkaline solution. This implies that the addition base is crucial to cyclic diaminophosphine oxides against hydrolysis in catalytic reaction in the presence of trace amount of water. Moreover, the effect of Neighboring Group Participation (N.G.P.) is presumed to account for the notable stability of preligand **1a** in basic condition.

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1. Introduction

The utilization of secondary phosphine oxides (SPOs: $\text{R}_1\text{R}_2\text{PH}(=\text{O})$) as preligands [1] to facilitate the formation of C–C, C–N and C–S bonds in transition metal complex catalyzed cross-coupling reactions was pioneered by Li et al. [2]. Various usages of SPO preligands have swiftly increased thereafter [3–7]. Secondary phosphine oxides (SPOs) are able to tautomerize to corresponding phosphinous acids (PAs: $\text{R}_1\text{R}_2\text{P}-\text{OH}$) in the presence of transition metal species (Scheme 1) [8], possibly via P–H insertion to transition metal centre then followed by proton transfer back to phosphoryl oxygen ($\text{P}=\text{O}$) of SPO [9].

It is known that most of SPOs are air- and moisture-stable species while the central phosphorus atom is in pentavalent state. This character enables its long-term storage and easy handling in bench operation [6j,10]. Typically, SPO is a thermodynamically much

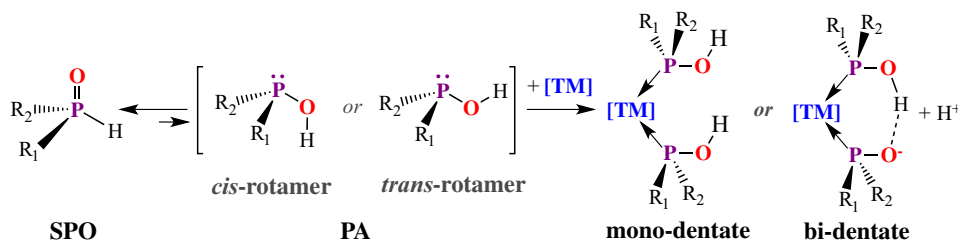
stable form than its PA tautomer [11], and therefore is the solo or major species that could be identified in solution [12]. Nevertheless, a few examples of PA tautomer, such as $(\text{CF}_3)_2\text{P}-\text{OH}$ including *cis*- and *trans*-rotamers, were reported and characterized by two neighboring gas-phase IR stretching modes for $-\text{OH}$ group at around 3600 cm^{-1} (Scheme 1) [13].

Borner and co-workers illustrated that solvent molecules with both good hydrogen-bond accepting ability and large polarity favor the formation of PA [14]. In addition, two solid-state structures of PA with two EWGs such as $-\text{C}_2\text{F}_5$ or $-\text{C}_6\text{F}_5$ were successfully determined [15]. In addition to the media polarization and electronic effect of substituents on the tautomeric equilibrium (Scheme 1), it has also been demonstrated that large steric hindrance of substituents could have more contribution on forming SPO species in the tautomeric equilibrium [16]. It could be associated with the increased basicity of phosphorus atom in the enlarged cone angle of PA [17].

Besides long-term preservation and convenient operation, SPO preligands have several specific benefits. In general, SPO is

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Scheme 1. Tautomerization of SPO in the presence of transition metal species.

relatively easy to synthesize [1]. PA tautomer of SPO is a weak Arrhenius acid [18], thus PA can be deprotonated to an electron-rich anionic phosphinito ligand (PA^- : $\text{R}_1\text{R}_2\text{P}-\text{O}^-$ in Scheme 2a) by eliminating a proton. The electron-donating ability of (PA^-) is superior to its neutral counterpart PA [19]. If two PA^- ligands coordinate to the same transition-metal center (TM), either $\text{TM}(\text{L}_{n-2})(\text{PA})_2$ or $\text{TM}(\text{L}_{n-2})(\text{PA}-\text{PA}^-)$ complexes can be obtained [10,20]. Also, $\text{TM}(\text{L}_{n-2})(\text{PA}-\text{PA}^-)$ can be regarded as a complex coordinated by two PA ligands, which undergoes self-assembly via the formation of an intramolecular hydrogen-bond interaction ($\text{PA}-\text{PA}^-$: $\text{R}_1\text{R}_2\text{P}-\text{O}^- \cdots \text{HO}-\text{PR}_1\text{R}_2$ in Scheme 2b) [1,21]. Therefore, the anionic bidentate ligating system enforces *cis*-form complex and gives rise to electron-rich transition metal centre [19]. The acidic proton remaining in the anionic bidentate ligating system of ($\text{PA}-\text{PA}^-$) can be deprotonated further, ultimately yielding two anionic monodentate ligands in $\text{TM}(\text{L}_{n-2})(\text{PA}^-)_2$ [19].

The deprotonated $\text{P}-\text{O}^-$ moiety of PA^- has been shown to be able to act either as a η^2 -ligand [23] or an ambidentate ligand [24]. The former type of PA^- has been applied on catalytic reaction of selectively heterolytic hydrogenation on carbonyl group versus alkene site when a pack of air-stable SPO-based gold nanoparticles is employed as catalyst (Scheme 2a) [22]. On the other hand, the anionic bidentate ligating system of $[\text{R}_1\text{R}_2\text{P}-\text{O}^- \cdots \text{HO}-\text{PR}_1\text{R}_2]$ has been assumed to be involved in heterolytic dehydrogenation process in protic solvent (Scheme 2b) [5d]. Moreover, Ustynyuk et al. based on theoretical studies also predicted that the reversible intramolecular proton transfer within the $[\text{R}_1\text{R}_2\text{P}-\text{O}^- \cdots \text{HO}-\text{PR}_1\text{R}_2]$ framework is valuable for adjusting the electron density in the course of platinum-catalyzed hydroformylation reactions [25].

Recently, air-stable $\text{O}-\text{P}-\text{O}$ and $\text{N}-\text{P}-\text{N}$ type cyclic heteroatom-substituted secondary phosphine oxides have been shown to be efficient preligands for bond activation of originally inactivated $\text{C}-\text{OTs}$, $\text{C}-\text{Cl}$, $\text{C}-\text{F}$, or $\text{C}-\text{H}$ bond in various catalytic cross-coupling reactions (Fig. 1) [5c,6e,j,26]. Applications of these HASPOs toward transition metals complexes based asymmetric catalysis have also been reviewed [27].

Actually, $\text{P}-\text{N}$ bond hydrolysis is a ubiquitous chemical transformation. For example, it has been shown to be a practical approach for synthesizing new compounds or making molecules with biological activity. $\text{P}-\text{N}$ bond hydrolysis can be employed to synthesize SPO [13c,28–30] or to control the growth of PdSe nanorod morphology [31]. $\text{P}-\text{N}$ bond hydrolysis can also be found in living systems. For instance, dephosphorylation concerning $\text{P}-\text{N}$ bond cleavage of phosphoamino acids is an essential biological reaction for cell signaling and functioning [32]. $\text{P}-\text{N}$ bond hydrolysis catalyzed is faster in an acidic environment than in neutral. In the case of $\text{P}-\text{N}$ bond hydrolysis of hexamethylphosphoramide (HMPA), no degradation was observed under neutral condition in the duration of 6 months [33].

Previous experimental observations revealed the swift decomposition of three HASPO **1a** [34a] analogs, those are **1d** [34b], **1e** [34a], and **1f** [34a], in reaction. Spilling and co-workers suggested a hydrolysis process taking place for the latter two

compounds; yet, without further detailed investigation [34a]. As for **1c**, the fast degradation rate generates difficulties for its bench operation and shelf storage [34a]. By contrast, opposite observation was documented in another literature which stated that **1c** could be stable for a few weeks against hydrolysis at room temperature [29]. Even in up-to-date *Communications* [24] and *Reviews* [5c,6e,27b,c], the (chiral) cyclic diaminophosphine oxide preligands are still regarded as both air- and moisture-stable compounds. However, we report herein that cyclic diaminophosphine oxide preligands, **1a** and **1b** (Fig. 2), are moisture-unstable and susceptible to hydrolysis.

The hydrolysis mechanism of four-coordinate phosphorus $\text{R}_2\text{P}(\text{=O})(\text{LG})$ has been categorized as $\text{S}_{\text{N}}2@P4$, which is coined by Bickelhaupt in their computational studies [35]. The symbol $\text{S}_{\text{N}}2@P4$ stands for a bimolecular nucleophilic-substitution reaction via a five-coordinate transition state (TS). For phosphorus acid amides, $\text{R}(\text{NR})\text{PH}(\text{=O})$, this mechanism is termed $\text{S}_{\text{N}}2\text{I}@P4$, and the intermediate given by the intra-molecular proton-transfer elementary reaction is due to the presence of $-\text{NR}_2$ functional group in $\text{R}(\text{NR})\text{PH}(\text{=O})$ [36]. Accordingly, HASPO **1a** and **1b** with the general formula of $(\text{RN}^i\text{NR}^j)\text{PH}(\text{=O})$ could be hydrolyzed via both $\text{S}_{\text{N}}2@P4$ (Scheme 3a) and $\text{S}_{\text{N}}2\text{I}@P4$ (Scheme 3b) mechanisms, respectively. As to $\text{S}_{\text{N}}1@P4$ mechanism, Borch and co-workers have recently shown that the heterolytic breakage of the $\text{P}-\text{N}$ bond in HMPA is too energy-demanding to proceed [37].

Herein, we report the results of investigation of the hydrolysis of **1a** and **1b** through $\text{S}_{\text{N}}2@P4$ and $\text{S}_{\text{N}}2\text{I}@P4$ -like pathways by computational methods along with detailed ^{31}P NMR studies. The objectives of this work are to understand the chemical reactivities of these cyclic $\text{N}-\text{P}-\text{N}$ type HASPOs toward moisture and how to prevent hydrolysis to occur. We believe that it is critical for the application of this cyclic $\text{N}-\text{P}-\text{N}$ type HASPOs in relevant catalysis.

2. Results and discussion

The cyclic $\text{N}-\text{P}-\text{N}$ type HASPO, secondary phosphine oxides **1a** [34a,38] and **1b** [6m] were synthesized and characterized according to the literature. Moisture stability of **1a** and **1b** were studied by means of ^{31}P NMR experiments at designated temperature according to the following procedure. Firstly, 0.1 mmol HASPO **1a** (or **1b**) was loaded into an air-tight NMR tube containing 0.5 mL *d*-solvent. Subsequently, 0.4 mmol D_2O or H_2O was added. With 2.0 M H_3PO_4 sealed in a capillary tube as the internal standard, ^{31}P NMR experiments were conducted at 55 °C in chloroform-*d* or at 90 °C in toluene-*d* [8]. ^{31}P NMR data were collected at selected time intervals. In order to scrutinize the pH-sensitivity regarding the HASPO hydrolysis rate, 0.12 equivalents of HCl or 0.18 equivalents of NaOH was also used to conduct the ^{31}P NMR experiments. DFT calculations were also employed to assist the elucidation of the plausible reaction mechanisms of consecutively double hydrolysis for HASPO **1b** and **1c** in neutral reaction condition. The results presumably will be beneficial for the clarification of the reactivity and the succeeding molecular design for cyclic $\text{N}-\text{P}-\text{N}$ type HASPOs as preligands.

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