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ARTICLE

Diazaphosphinanes as Hydride, Hydrogen-atom, Proton or Electron Donors under Transition-metal-free Conditions: Thermodynamics, Kinetics, and Synthetic Applications

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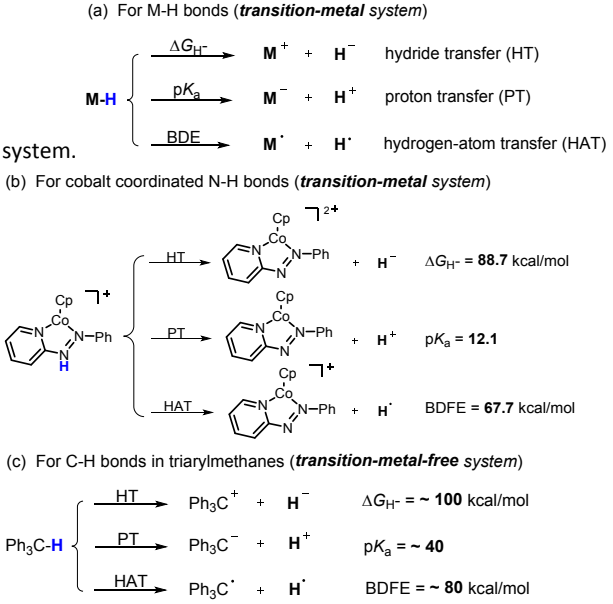
Jingjing Zhang,[a] Jin-Dong Yang,[a]* Jin-Pei Cheng[a,b]*

Exploration of new hydrogen donors is in large demand for hydrogenation chemistry. Herein, we developed a new 1,3,2-diazaphosphinane **1a**, which can serve as a hydride, hydrogen-atom or proton donor without transition-metal mediation. The thermodynamics and kinetics of these three pathways of **1a**, together with those of its analog **1b**, were investigated in acetonitrile. Noteworthily, the reduction potentials (E_{red}) of the phosphenium cations **1a-[P]**$^+$ and **1b-[P]**$^+$ are extremely low, as being -1.94 and -2.39 V (vs. $Fc^{+/0}$), respectively, enabling corresponding phosphinyl radicals to function as neutral super-electron-donors. Kinetic studies revealed an extraordinarily large kinetic isotope effect KIE(**1a**) of 31.3 for the hydrogen-atom transfer from **1a** to 2,4,6-tri-(tert-butyl)-phenoxyl radical, implying a tunneling effect. Furthermore, successful applications of these diverse P-H bond energetic parameters in organic syntheses were exemplified, shedding light on more exploitations of these versatile and powerful diazaphosphinane reagents in organic chemistry.

Introduction

Hydrogen transfer plays a very important role in chemical science and related fields. This process occurs through cleavage of the targeted R-H bond in three possible pathways (Scheme 1), *i.e.*, hydride (H^-)[1], hydrogen-atom ($H^•$)[2] and proton (H^+)[3] transfers, which, from thermodynamic aspect, depends on the R-H bond strength and the nature of the atom bound to the transferred hydrogen. Accordingly, knowledge of the relevant thermodynamics of hydricity ΔG_{H^-},[1b, 1c, 4] bond-dissociation free-energy BDFE[5] and acidity pK_a[3c, 6] as well as the kinetics[7] relevant to these processes would facilitate rational exploitations of new transformations. In recent years, considerable attention has been paid on developing new hydrogen sources with versatile hydrogen donor reactivities, with particular interests in transition-metal hydrides M-H[1c], such as hydrogenase enzyme analogs[8] and hydrogenation catalysts[9], and main-group organic hydrides X-H,[1b] such as nicotinamide coenzyme models[10] and Hantzsch esters[11], and so on.

It is well known that metal hydrides (M-H) could serve as H^-, $H^•$ and H^+ donors (Scheme 1a).[1c, 12] Their diverse hydrogen reactivities originate from the readily-modulated polarity of M-H bonds through electronic communication between the metal centers and coordinated ligands. Compared to an M-H system, the X-H hydride manifested some advantages in mild reaction conditions, good functional-group compatibility, easy modification, etc. Integration of these three dissociation possibilities into one X-H covalent bond is of a substantial challenge, due to the great disparity in their electronegativity of the X and H fragments. Nevertheless, Waymouth *et al*. very recently reported an excellent new example of such X-H bond where the N-H bond of the phenylazopyridine ligand in Co(I) complex can serve as either a H^-, $H^•$ or a H^+ donor (Scheme 1b).[13] It is noted, however, that the diverse reactivity of this N-H bond may have to require a latent electronic communication between the azopyridine ligand and cobalt within the five-membered ring, so it may be viewed as a quasi-M-H system.



Scheme 1. Possible pathways of hydrogen transfers for transition-metal and transition-metal-free systems as well as corresponding thermodynamic driving forces in acetonitrile.

[a] *Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing 100084, China.*
[b] *State Key Laboratory of Elemento-organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.*
† Footnotes relating to the title and/or authors should appear here.
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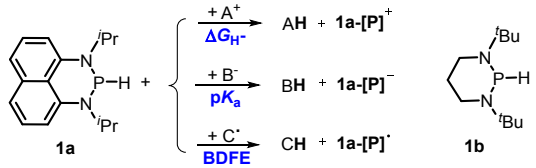
For a true transition-metal-free system, till present only the triarylmethane analogs, where exist steric as well as resonance stabilization effects on the incipient radical or charges, were reported to have the α-C-H bond-cleavage energies determined for all the three pathways (Scheme 1c).[14] However, their poor hydrogen donability and severe steric hindrance make these dissociation processes not too much useful for synthesis. This, instead, stimulated our interest to find out more useful transition-metal-free X-H systems that promise both the desired energetic measurement and new synthetic applications.

Recently, diazaphospholenium hydrides (P-H) have attracted substantial research activities due to their super hydricity endowed by the unique diazaphospholene skeleton.[15] Many diazaphospholenes were developed and successfully used in various hydridic reductions.[16] However, the superior hydricity made their other promising applications, such as serving as hydrogen-atom and proton donors, as well as the precursors of the strong electron donors, greatly overlooked. Considering the similar electronegativity of the hydrogen (χ^{AR} = 2.20) and phosphorus (χ^{AR} = 2.06) atoms,[15b] we reckoned that the P-H bond, beside as a good hydride donor,[17] may have the potential to release proton and hydrogen-atom[18] as well, by fine-tuning its electrical properties of the P fragment. And indeed lucky enough, this was realized in the present work.

Herein, we reported a new *N*-heterocyclic phosphine **1a**, which could act as a H^-, $H^\bullet$ and H^+ donor (Scheme 2). Thermodynamics and kinetics pertinent to these three processes were examined in details. For comparison, **1b** was investigated as well. Based on the P-H bond energetic studies, we also exploited their versatile applications in the reduction of pyridines, synthesis of bisphosphines, H/D exchange, and activation of carbon-halogen bonds as original examples.



Scheme 2. P-H reagents **1a** and **1b** serving as diverse hydrogen donors. **A**$^+$, **B**$^-$ and **C**$^\bullet$ are the hydride, proton and hydrogen-atom acceptors, respectively.

Results and Discussion

Synthesis. Substrate **1a** was prepared via H/Cl exchange between the corresponding phosphoric chloride and $LiAlH_4$ in THF according to literature[15, 17] (see Supporting Information SI for details). $LiAlD_4$ was used for deriving the deuterated substrates **1a-D** and **1b-D**. The crystal structure of **1a** was identified as in Figure 1 that features an envelope configuration with the P atom standing out of the naphthalene plane and the P-H bond adopting a flagpole position, similar to the five-membered ring analogs disclosed previously.[15a] And the P-H distance of 1.42(2) Å is slightly shorter than the five-membered ring analog.[15] ^{31}P NMR of **1a** in CD_3CN shows a *dt* peak at 25.66 ppm that is split by the hydrogens on the P atom and isopropyl groups. It moves to the higher magnetic field in comparison with other *N*-heterocyclic phosphines.[17] Under inert atmosphere, **1a** is stable enough for over 12 hours in tetrahydrofuran, acetonitrile, alcohols, toluene, dimethylsulfoxide and chloroform. On the other hand, **1b** is stable in these solvents as well except in alcohols and chlorinated hydrocarbons, where it decomposed rapidly to yield phosphonites $(RO)_2PH$[19] or 2-chloro-1,3,2-diazaphosphinane [P]-Cl (Scheme 3), showing that **1b** is more air- and moisture-sensitive than **1a**.

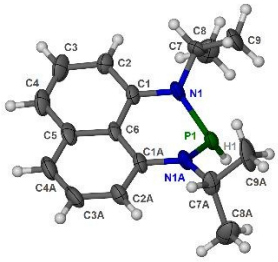
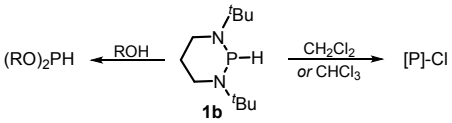


Figure 1. The crystal structure of **1a** (50% probability thermal ellipsoids).[20] Selected bond lengths (in Å): P1-H1 1.42(2), P1-N1 1.747(6), N1-C1 1.329(9), N1-C7 1.440(8), C1-C6 1.413(8).

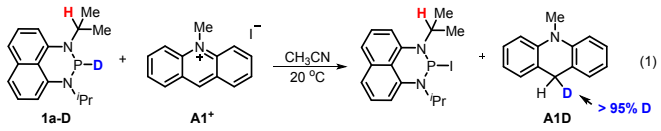


Scheme 3. Decomposition of **1b** in alcohols and chlorinated hydrocarbons. [P] = $(CH_2)_3(N^tBu)_2P$, R = Me or Et.

Redox property. The oxidation potentials of **1a** and **1b** were examined by cyclic voltammetry (CV), exhibiting a partially reversible oxidation peak of **1a** to **1a**$^{\bullet+}$ at 0.23 V (vs. $Fc^{+/0}$, Figure S1a) and an irreversible oxidation wave of **1b** at 0.47 V (vs. $Fc^{+/0}$, Figure S1b) in acetonitrile. The low oxidation potentials of **1a** and **1b** indicate their good reducing capacity. It is interesting to find that **1a** is a better electron donor, in spite of being a far poorer hydride donor than **1b** (*vide infra*). Besides, the redox behaviors of the respective phosphinyl radicals (**1a-[P]**$^\bullet$ and **1b-[P]**$^\bullet$) were also examined through the reduction of the corresponding phosphenium cations (**1a-[P]**$^+$[21] and **1b-[P]**$^+$), giving the CV peaks at -1.94 V and -2.39 V (vs. $Fc^{+/0}$) in acetonitrile, respectively (Figures S1c and 1d). The extremely low potentials, especially for **1b-[P]**$^+$, indicate the very high reducing capacity of the corresponding **1a-[P]**$^\bullet$ and **1b-[P]**$^\bullet$ radicals. This suggests that they both have a very promising potential to serve as a super electron donor in organic synthesis to reduce aryl halides.[22] And indeed, this was verified in the tentative application of the present work in radical hydrodebromination of bromobenzene (see Application part, *vide infra*).

Thermodynamic driving force and reactivity. *Hydride Transfer (HT).* Hydride transfer from **1a** or **1b**[17] to *N*-methylacridinium iodide **A1**$^+$ yielded equimolar products (Figure S3). To exclude the suspected interruption of the hydridic isopropyl α-C-H, the deuterated substrate **1a-D** was employed, and over 95% deuterated **A1D** was

derived (Eq. 1 and Figure S4). This confirmed that the P-H hydride of **1a** is a stronger donor than that of the isopropyl α-C-H.

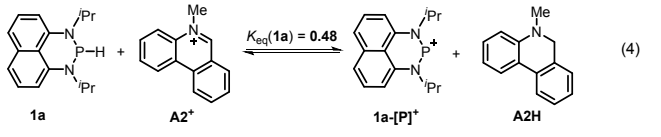


1a-D A1+ A1D (1)

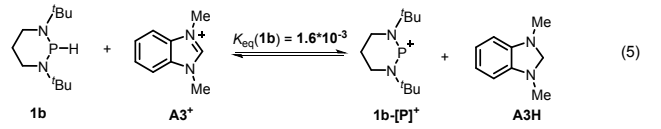
The hydricity (ΔG_H-, defined by Eq. 2) of **1a** and **1b** in acetonitrile was determined by measuring their equilibrium constants with the acceptors of known hydricities (Eq. 3). For example, the measured hydride transfer equilibrium constant K_{eq}(**1a**) of 0.48 (equivalent to 0.43 kcal/mol) between **1a** and phenanthridinuim trifluoromethanesulfonate **A2**$^+$ (ΔG_H-(**A2H**) = 61.4 kcal/mol)[1b] provided the hydricity ΔG_H- of **1a** to be 61.8 kcal/mol (see Figure S5 in SI for details) and other equilibria (in Figure S6 and S7) verified this value, giving a mean hydricity of 62.2 ± 1.0 kcal/mol. This finds **1a** to be a moderate hydride donor, close to the hydride-donating ability of the NADH analogs.[1b] Thus, it should be capable of reducing the commonly-used hydride acceptors, such as *N*-methylacridinium cation (ΔG_H- = 76 kcal/mol), 9-phenylxanthylium cation (89 kcal/mol) and trityl cation (99 kcal/mol). Similarly, the much lower equilibrium constant K_{eq}(**1b**) of 1.6 × 10^{-3} (equivalent to 3.8 kcal/mol, Eq. 5 and Figure S8) established between **1b** and benzimidazolium perchlorate **A3**$^+$ (ΔG_H-(**A3H**) = 45.0 kcal/mol)[4b] rendered ΔG_H-(**1b**) to be 48.8 ± 1.0 kcal/mol, which is comparable to that of the commonly used good hydride donor 2,3-dihydrobenzo[*d*]imidazoles.[1b] The good hydridic reactivity of **1b** was illustrated in our recent work in reduction of various unsaturated compounds.[17] It is interesting to note that **1b** is about 13 kcal/mol stronger than **1a** in hydricity, but is 0.24 V weaker in electron-donating ability.

(2)

$$\Delta G_{rxn} = -RT\ln K_{eq} = \Delta G_H\text{-}(\mathbf{1}) - \Delta G_H\text{-}(\mathbf{AH}) \quad (3)$$

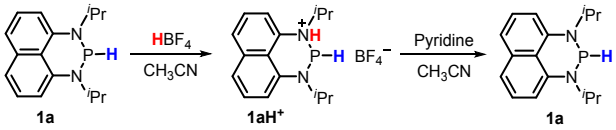


1a A2+ 1a-[P]+ A2H (4)



1b A3+ 1b-[P]+ A3H (5)

The hydricity can be used to rationalize the disparate reactivity between **1a** and some reported diazaphospholenium hydrides. The latter compounds were reported to react with strong acid HBF_4 to give H_2 and the corresponding phosphenium cations.[15b] However, when **1a** was treated with HBF_4 (or HOTf), no gaseous product was generated. Instead, a new phosphorus species with a doublet peak at about 80 ppm was detected in ^{31}P NMR spectrum (Figure S9a and S9b). To identify this newly formed species, a base pyridine was added to the reaction mixture, which rendered **1a** as the primary product with a small amount of unidentified impurities (Figure S9c). Consequently, this mysterious P species was speculated to be protonated **1a** (**1aH**$^+$, Scheme 4). Based on the doublet peak of the phosphorus atom in ^{31}P NMR (if the extraneous proton connected to the P atom, a triplet ^{31}P peak would be observed otherwise) and the unsymmetrical peaks of naphthyl and isopropyl hydrogens in ^{1}H NMR (Figure S10), the protonated site was thus assigned to the *N* atom (Scheme 4). We thought that their dissimilarity in reactivity between **1a** and some reported diazaphospholenium hydrides should originate from the relatively weak hydricity of **1a** (ΔG_H- = 62.2 kcal/mol). As a consequence, it makes the H_2-release unable to compete with its protonation even under the condition of heating (80 °C for 5 hours). The moderate hydricity of **1a** endows it with good tolerance to even strong acids, avoiding direct elimination of dihydrogen. This in turn offers a possibility for **1a** to act as a hydride donor in acid-catalyzed reduction. Lots of examples in this connection[1a] can be found especially in hydrogenation of imines by hydride donors with comparable hydricity to **1a** (~ 60-70 kcal/mol, like Hantzsch ester,[23] benzothiazoline[24] and cyclohexadiene[25]) under the catalysis of Brønsted acids (for examples BINOL–phosphoric acid, trifluoroacetic acid and Tf_2NH).



1a 1aH+ 1a

Scheme 4 Protonation of **1a** by HBF_4, and recovery of it by adding pyridine in CD_3CN.

The kinetics of the hydride transfer from **1a** to **A1**$^+$ was conducted by following the decay of the absorption of **A1**$^+$ in CH_3CN at 430 nm with stopped-flow spectrophotometer (Figure 2, see SI for details). The second-order rate constant k_{HT}(**1a**) was found to be 5.94 M^{-1} s^{-1} (Inset in Figure 2 and Table S1). Moreover, the nucleophilicity of **1a** can be estimated by the second-order rate constant of the reaction of **1a** with **A1**$^+$. Because **1a** has a similar structure with **1b**, based on the nucleophile-specific sensitivity parameter s_N of **1b** (0.52) and the electrophilicity of **A1**$^+$ in our recent work,[17] the nucleophilicity *N* of **1a** is estimated as 8.64. Similarly, the kinetics of **1a-D** with **A1**$^+$ k_{HT}(**1a-D**) was determined to be 2.34 M^{-1} s^{-1} (Table S2). These gave a primary kinetic isotope effect KIE [k_{HT}(**1a**)/k_{HT}(**1a-D**)] of 2.5. A comparison with the previously determined k_{HT}(**1b**) of 5.41 × 10^2 M^{-1} s^{-1} for the reaction of **1b** with **A1**$^+$ in our earlier work[17] indicates that **1b** is about 100 times more reactive than **1a**. This is exactly in accordance with the order of their hydricities (ΔG_H-) of **1a** vs. **1b** found here.

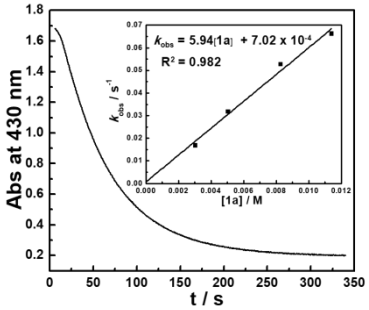


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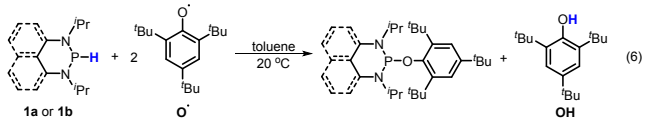
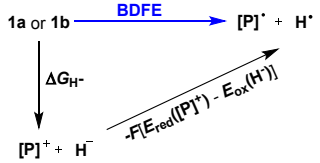
Figure 2. Monoexponential decay of the absorbance *Abs* (at 430 nm) with the time *t* (s) for the reaction of **1a** (3.03×10^{-3} M) with **A1**$^+$ (5.00×10^{-5} M) in CH_3CN at 20 °C. Inset: Correlation of k_{obs} with [**1a**].

Hydrogen-atom Transfer (HAT). To examine the possibility of a HAT reaction from diazaphosphinane substrates **1**, the reactions of **1a** and **1b** with the 2,4,6-tri-tert-butyl-phenoxyl radical **O•** were conducted, and yielded 2,4,6-tri-*tert*-butylphenol **OH** and the corresponding phosphorus species (Eq. 6) without generation of bisphosphines (compared to the reaction of **1a** or **1b** with AIBN, Table 1). Stoichiometric study found a [**1**]/[**O•**] ratio of 1:2, consistent with the product analysis (Figure S11 and S12).



(6)

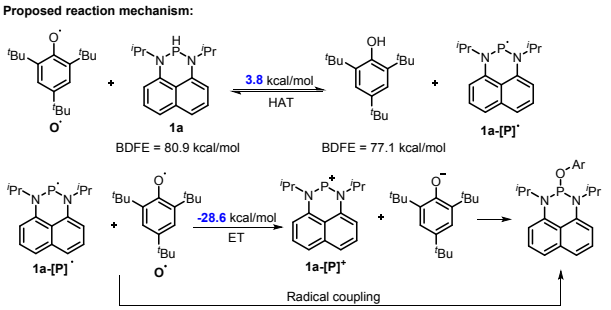
To evaluate the hydrogen-atom donability of diazaphosphinanes (*i.e.*, P-H BDFE), the thermodynamic cycle was applied on the basis of the ΔG_H- and E_{red}(**[P]**$^+$) in hand (Scheme 5 and Eq. 7; FE_{ox}(**H**$^-$) is -26.0 kcal/mol[1c] in acetonitrile vs. $Fc^{0/+}$).[26] Substituting the known values into Eq. 7[26a, 27] gives the P-H BDFEs of 80.9 ± 2.0 and 77.9 ± 2.0 kcal/mol for **1a** and **1b**, respectively, being comparable with those of phenol and thiophenol antioxidants. Therefore, they could transfer hydrogen-atom smoothly to acceptors with X-H BDFEs around or larger than 78 kcal/mol, such as 2,4,6-tri-tert-butyl-phenoxyl **O•** (77.1 kcal/mol), $CN(CH_3)_2C^•$ (about 88 kcal/mol) and phenyl radicals (104.7 kcal/mol).[5b, 28] Compared to **1b**, though the fused aryl groups attenuate the hydricity of **1a** by 13 kcal/mol thermodynamically, they show negligible effect on the HAT reactivity.



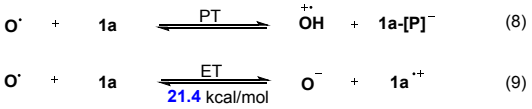
Scheme 5. Thermodynamic cycle for deriving the P-H BDFEs of **1a** and **1b**.

$$BDFE = \Delta G_{H^-} - F(E_{red}([\mathbf{P}]^+) - E_{ox}(\mathbf{H}^-))$$
$$= \Delta G_{H^-} - 23.06E_{red}([\mathbf{P}]^+) - 26.0 \quad \text{(kcal/mol)} \quad (7)$$

The reaction mechanism of **1a** with radical **O•** (Eq. 6) was proposed in Scheme 6 based on the derived thermodynamic data (the reaction of **1b** with **O•** is similar). Since hydrogen-atom transfer from **1a** to **O•** is slightly endothermic (~ 4 kcal/mol), it implies the possibility for a reversible HAT. This reversible HAT could be further driven to the far right by the largely exothermic electron transfer ET of **1a**-**[P]•** radical (E_{ox}(**1a**-**[P]•**) = -1.94 V) or a follow-up radical coupling. The observed stoichiometric ratio of 1:2 for the reactants [**1**] vs. [**O•**] is in exact accordance with the HAT mechanism proposed. On the other hand, a suspected proton transfer between **1a** and the **O•** radical can be easily ruled out due to the very weak acidity of **1a** (*vide infra*) and strong acidity (pK_a of ~ -3)[5b] reported for the phenol radical cation (Eq. 8). The other suspected possibility, *i.e.* the ET path between **1a** and the **O•** radical (E_{red} = -0.70 V[5b]) can also be excluded by the similar strategy on the basis of their respective thermodynamics determined, that indicates the ET from **1a** to **O•** is remarkably uphill (ΔG_{ET} = 21.4 kcal/mol, Eq. 9).[13, 29] It is thus safe to conclude that the initial HAT should be the rate-determining step (RDS) for the reaction expressed in Eq. 6.



Scheme 6. The possible mechanism for the reaction of **1a** with **O•**. Ar = 2,4,6-tri-*tert*-butyl-phenyl group.

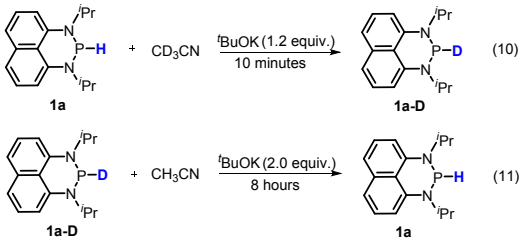


The rate constants of this hydrogen-atom transfers from **1a** and **1a-D** to radical **O•** were measured to be k_{HAT}(**1a**) of 0.70 M^{-1} s^{-1} and k_{HAT}(**1a-D**) of 2.24×10^{-2} M^{-1} s^{-1}, respectively (Tables S3 and 4). This intermediately points out an extremely large KIE(**1a**) of 31.3, implying a tunneling effect in this HAT process. Such a large KIE has been found in biochemical[30] and transition-metal systems[31], but seldom observed in organic HAT processes. Similarly, the rate of the analogous HAT of **1b** k_{HAT}(**1b**) was determined as 0.74 M^{-1} s^{-1} (Table S5). The quite close k_{HAT} for **1a** and **1b** agrees well with their comparable P-H BDFEs (80.9 vs. 77.9 kcal/mol, *vide supra*), verifying their similar HAT reactivity. However, the same kinetic study for **1b-D** gave a k_{HAT}(**1b-D**) of 0.12 M^{-1} s^{-1} (Table S6), rendering a primary KIE(**1b**) of 6.2 with no tunneling phenomenon detected.

To understand this discrepancy, the temperature-dependent kinetics were further performed (Tables S7-10). The ratio of Arrhenius pre-factors [A(**1a**)/A(**1a-D**)] was obtained as 0.021, and the activation energy difference [E_a(**1a**) - E_a(**1a-D**)] was -5.53 kcal/mol (Figure S2 and Table S11). These kinetic characteristics [A(**1a**)/A(**1a-D**) << 1, and E_a(**1a**) - E_a(**1a-D**) << 0] are in fact in line with the tunneling model illustrated by Klinman,[30a] which features a "through-the-barrier" transition state near the top of the classical barrier. In the **1b** system, on the other hand, the normal primary KIE of 6.2, A(**1b**)/A(**1b-D**) of 3.39 and [E_a(**1b**) - E_a(**1b-D**)] of -0.38 kcal/mol all support a classical "over-the-barrier" transition state. A more comprehensive investigation of the tunneling issue is presently underway.

Proton Transfer (PT). It's known that a good hydride donor usually exhibits poor acidity. This explains why the acidity of widely-used X-H type hydride donors, e.g. 2,3-dihydrobenzo[*d*]-imidazoles, have never been determined in the absence of metal-coordination. The hydricity of the present *N*-heterocyclic phosphines is also quite

good (*vide supra*), hence investigation of their acidic reactivity cannot be expected too straightforward. Nevertheless, as learned from the initial failures in deprotonating **1a** or **1b** with some ordinary strong bases, such as 1,8-diazabicyclo[5,4,0]-7-undecene (DBU, pK_a = 24.34 in CH_3CN), 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (TBD, pK_a = 26.03) and (tert-butylimino)tris(pyrrolidino)-phosphorane (BTPP, pK_a = 28.42)[28] (see SI for details), we finally found that the H/D exchange of the **1a** P-H proton in the presence of stoichiometric ^{t}BuOK in CD_3CN (Eq. 10 and Figure S13) was accomplished in about 10 minutes at room temperature,[32] whereas the same operation for **1a-D** in CH_3CN finished in 8 hours at room temperature (Eq. 11 and Figure S14). The reversible H/D exchange of **1a** in acetonitrile under the promotion of ^{t}BuOK suggested that the acidity of **1a** reaches the measurable acidity limitation in acetonitrile (see SI for details).[33] As for **1b** with much stronger hydricity, its acidity is, unfortunately, too weak to examine in solution by any existing experiment. However, it is worth noting that the acidity of a P-H bond can be significantly enhanced upon activation by coordination with transition metals[34] or other Lewis acids.[35]

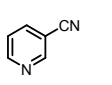
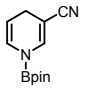
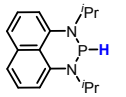
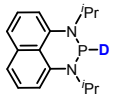
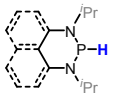
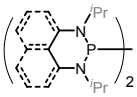


Applications in syntheses. Based on the above thermodynamic and kinetic investigations, the potential of applying **1a** and **1b** in organic syntheses, encompassing the diverse hydrogen (H^+, $H^\bullet$ and H^-) or electron transfer, was preliminarily explored and showcased herein.

Catalytic reduction of pyridines is a prevail strategy for synthesis of dihydropyridines. Recently, Kinjo *et. al.*[16g] *and* Speed *et. al.*[36] exploited 1,3,2-diazaphosphenium-catalyzed hydroboration of pyridines with good regio- and chemo-selectivity.[16g] However, in their system, the substrate 3-CN-pyridine gave a mixture of three dihydropyridine isomers. To our delight, we found that under the catalysis of 15 mol% our **1a-[P]$^+$**,[37] the sole 1,4-hydroborated isomer of this reaction was selectively produced in moderate yield 40% (entry 1 in Table 1 and Figure S15). The good region-selectivity may be ascribed to the steric factors of isopropyl group on the nitrogen atom of **1a** based on Kinjo's DFT calculations.[16g] This good regio-selectivity exhibits the catalytic potential of **1a** in the reduction of unsaturated compounds.

Moreover, the acidic character of **1a** (*vide supra*) offers a more economic way for the synthesis of deuterated reagent **1a-D** (entry 2 in Table 1) by employing the much cheaper deuterated solvent CD_3CN instead of expensive $LiAlD_4$ in almost quantitative yield (see SI for details about the synthetic method). Meanwhile, it also provides a new approach for isotope labeling of many other hydridic species. Generation of the hydridic hydrogen from a "protic" solvent as illustrated here may serve as an example of umpolung which was also proposed by Gudat *et al.* for P-H bond.

Table 1. Applications of **1a** and **1b** in organic syntheses.

Entry	Reactant	Condition	Product	Yield	Type
(1)		**1a-[P]$^+$** (15 mol%), HBpin (1.5 eq.) CH_3CN, 80 °C, 36 h		40%[a]	HT
(2)	 **1a**	^{t}BuOK, CD_3CN 20 °C, 10 min.	 **1a-D**	Quant.[b]	PT
(3)	 **1**	AIBN (1.5 eq.),C_6D_6 80 °C, 3 h	 **1-[P$_2$]**	> 90%[b]	HAT
(4)		**1b** (1.5 eq.), AIBN 15 mol% toluene-d_8, 90 °C, 5 h		> 90%[c]	HAT & ET

[a] Isolated yield. [b] NMR yields determined by the amount of phosphorus species. [c] NMR yeilds with 1,3,5-trimethoxybenzene as the internal standard.

Since bisphosphines can easily decompose into phosphinyl radicals,[38] they could serve as radical reservoirs for relevant studies and applications. Based on the thermodynamic analysis, $CN(CH_3)_2C^\bullet$ (C-H BDFE ≈ 85 kcal/mol), generated from homolysis of azo-bis-isobutyronitrile (AIBN), could abstract the hydrogen-atom from **1a** (P-H BDFE = 80.9 kcal/mol). Then, the generated phosphinyl radical **1a-[P]$^\bullet$** coupled quickly with each other to yield bisphosphines (entry 3 in Table 1, Figure S16 for **1a** and Figure S17 for **1b**). The targeted dimers[39] are readily extracted from reaction mixtures in a high yield. This transformation, together with Gudat's photochemical dehydrocoupling,[18] offers an easy access to bisphosphines, avoiding complicated and harsh operations and workups required in other synthetic processes using metals sodium[38d] and magnesium[38a-c].

Furthermore, we attempted to design a new radical transformation by an integrated use of hydrogen-atom and electron transfers from *N*-heterocyclic phosphines. This was inspired by the reactions of AIBN with **1a** and **1b**, where phosphinyl radicals can be easily generated from their P-H precursors through hydrogen-atom release. The very negative oxidation potentials of phosphinyl radicals imply their competency in the reduction of challenging substrates. If a substrate in the reaction system is sufficiently oxidative, its single-electron capture from phosphinyl radicals may be able to compete with radical coupling. In such cases, subsequent transformations may be triggered. Based on the redox potentials of **1b-[P]$^\bullet$** (E_{ox} = -2.39 V vs. $Fc^{+/0}$, the same with the E_{red}(**1b-[P]$^+$**)) and bromobenzene (E_{red} = -2.8 V)[40], hydrodehalogenation of bromobenzene by **1b** was performed in toluene with 15 mol% AIBN as the initiator (entry 4 in Table 1, Figure S18). After 5 hours, the expected reduction product benzene was obtained in over 90% yield. Due to the poor reduction ability of **1a-[P]$^\bullet$**, the reaction could not proceed when **1a** was used.[41] Therefore, it could be anticipated that these *N*-heterocyclic phosphines may open a promising avenue for the development of super electron donors.

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Conclusions

Hydrogen and electron transfers from phosphines **1a** and **1b** were thermodynamically and kinetically investigated in acetonitrile. The P-H bond of **1a** can participate in reactions involving formal transfer of a hydride/hydrogen-atom/proton to a substrate under respective conditions in the absence of the usually required transition-metal- or Lewis acid-mediation. It was observed that **1a** is a moderate hydride and hydrogen-atom donor, but a poor Brønsted acid. For comparison, **1b** is a good hydride donor and moderate hydrogen-atom donor; but did not show a detectable acidic reactivity even under strongest basic solution. As regard to electron donability, **1a** (E_{ox}(**1a**) = 0.23 V) is superior to **1b** (E_{ox}(**1b**) = 0.47 V), contrasting to the order of their hydridic reactivity. Their corresponding phosphinyl radicals are very strong electron donors as reflected by their extremely negative redox potentials. Kinetic studies revealed a tunneling contribution (KIE = 31.3) to the hydrogen-atom transfer from **1a** to the phenoxy radical. Based on the derived energetic parameters, their synthetic applications were tentatively exploited. Preliminary results from the synthetic attempts by using the new reagents **1a** and **1b** confirmed their competence as effective hydrogen and electron donors in various redox transformations. The effectiveness of applying the relevant physicochemical parameters in analysis and design of hydrogen transfer reactions was also convinced.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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41. DFT calculations showed **1a-[P]•** and **1b-[P]•** should have a comparable ability (with an energy difference of 1.3 kcal/mol, see SI for details) in abstracting bromine atom. This failed to explain the disparate yields of <10% for **1a-[P]•** and 90% for **1b-[P]•**. Besides, according to the redox potentials of **1b-[P]•** (E_{ox} = -2.39 V vs. Fc in MeCN) and bromobenzene (E_{red} = -2.8 V), the electron transfer from **1b-[P]•** to bromobenzene is a feasible reversible process, while that for **1a-[P]•** (E_{ox} = -1.94 V) is thermodynamically prohibited. These findings preferentially support an ET-initiated mechanism rather than a direct bromine abstraction.

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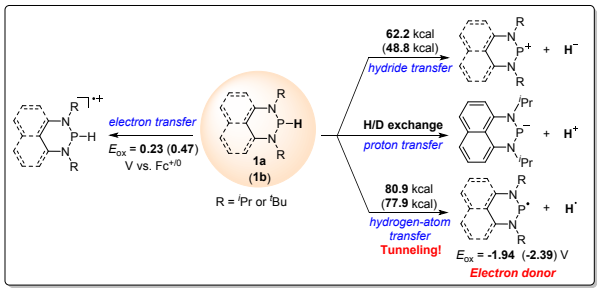

"3-in-1" diazaphospholenium hydride reagent: A new 1,3,2-diazaphosphinane, which can serve as a formal hydride, hydrogen-atom or proton donor without transition-metal mediation was exploited thermodynamically and kinetically. Kinetic studies imply a tunneling effect for the hydrogen-atom transfer process. The extremely low oxidation potentials of corresponding phosphinyl radicals enable them to serve as super electron donors in organic syntheses. And, the very promising potentials in versatile syntheses have been successfully demonstrated.