A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Title: Nucleophilicity Scale for the Reactivity of Diazaphospholenium Hydrides: Structural Insights and Synthetic Applications

Authors: Jingjing Zhang, Jin-Dong Yang, and Jin-Pei Cheng

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201901456
Angew. Chem. 10.1002/ange.201901456

Link to VoR: http://dx.doi.org/10.1002/anie.201901456
http://dx.doi.org/10.1002/ange.201901456

WILEY-VCH

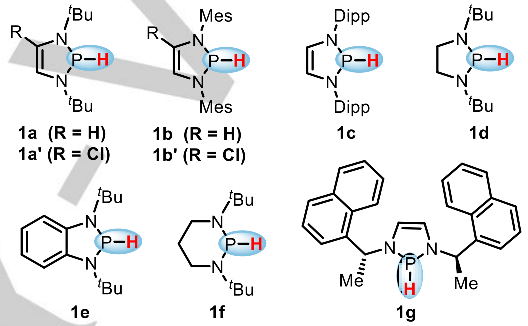
Nucleophilicity Scale for the Reactivity of Diazaphospholenium Hydrides: Structural Insights and Synthetic Applications

Jingjing Zhang, Jin-Dong Yang,* and Jin-Pei Cheng*

Abstract: *Nucleophilicity parameters (N, s_N) of a group of representative diazaphospholenium hydrides were derived by kinetic investigations of their hydride transfer to a series of reference electrophiles with known electrophilicity (E) values, using the well-established Mayr equation $\log k_2 = s_N(N + E)$. The achieved N scale covers over ten N units, ranging from the most reactive hydride donor (N = 25.5) to the least of the scale (N = 13.5). This immediately discloses the highest N value ever quantified in terms of Mayr's nucleophilicity scales reported previously for neutral transition metal-free hydride donors, and hence, implies an exceptional reactivity of this reagent. Even the least reactive hydride donor of this series is still a better hydride donor than those of many other popular types of nucleophiles such as the C-H, B-H, Si-H and transition metal M-H hydride donors. Structure–reactivity analysis reveals that 2-H-1,3,2-diazaphospholene's outstanding hydricity is benefited from the unsaturated skeleton.*

Contrasting to the well-known protic reactivity of conventional P-H bonds,[1] 2-*H*-1,3,2-diazaphospholene **1a** (Figure 1) exhibits a peculiar hydridic propensity, as endowed by its unique diazaphospholene skeleton.[2] This unexpected P-H bond philicity leads to an inverted regioselectivity and opens new applications of phosphines in organic synthesis. Gudat and co-workers' seminal work demonstrated that **1a** is a sort of super-hydride,[3] yet with common features of organic reagents,[4] such as relatively low cost and good solubility in organic media. These advantages make synthetic applications of the P-H hydrides a burgeoning field. Consequently, a number of *N*-heterocyclic phosphorus hydrides (Figure 1) and their analogues have been developed in recent years, rendering many originally infeasible reactions to occur under metal-free conditions, such as reductions of polar olefins,[5] imines,[5a] ketones[6] and azocompounds,[7] valorization of CO_2,[8] and hydroboration of pyridines[9]. Moreover, their chiral analogs (like **1g**) were also exploited in catalysis of asymmetric hydride-initiated transformations with high enantioselectivity.[10] In these processes, the propensity of P-H species to cleavage their P-H bonds dominates the feasibility of the reaction.

Despite the wide applications of this new group of strong hydrides in syntheses, further extending their utility to find new synthetic methodologies or to explore new highly efficient P-H reagents is, inevitably, hampered by a bottleneck, that is, lack of a quantitative understanding of the structure-reactivity relationship. In this regard, and also, based on our expertise in this area,[11] we have carried out a systematic kinetic study, aiming to establish a reactivity scale for the typical group of diazaphospholenium hydrides illustrated in Figure 1. This scale can then be used to quantify their hydride-donating abilities and disclose structural insights behind the data that is meaningful for guiding further investigation. Hence, here in this work, the first quantitative measurements of the nucleophilicity (*N*) parameters of the P-H hydrides have been conducted, based on the Mayr equation [eq. (1)].



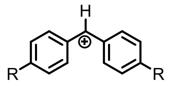
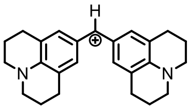
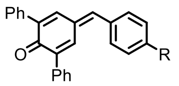
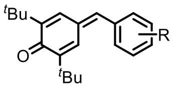
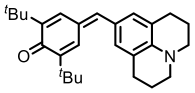
1a (R = H)
1a' (R = Cl)
1b (R = H)
1b' (R = Cl)
1c
1d
1e
1f
1g

Figure 1. Commonly used diazaphospholenes **1** with Mes = 2,4,6-$Me_3C_6H_2$ and Dipp = 2,6-$^iPr_2C_6H_3$.

According to Mayr's three-parameter equation [eq. (1)],[12] the hydridic reactivity of these P-H reagents **1a-f** can be described by the nucleophilicity parameters *N*, together with a nucleophile-specific sensitivity factor s_N, derived from their rate constants with a series of reference electrophiles of known eletrophilic parameters (*E*). In the present work, benzhydrylium ions[13] and quinone methides[14] were taken as the electrophiles, whose *E* vaues and the respective maximum absorptions (λ_{max}) are presented in Table 1.

$$\log k_2\,(20\ °C) = s_N(N + E) \qquad (1)$$

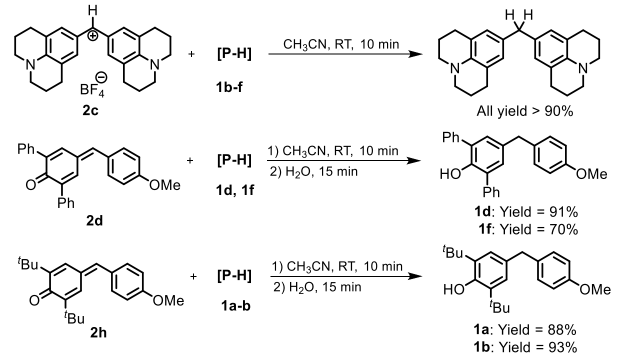
Table 1. Benzhydrylium ions **2a–c** (BF_4^- salts) and quinone methides **2d-i** employed as reference electrophiles in this work.

Electrophiles			*E*	λ_{max}(nm)
	R = NMe_2	**2a**	-7.02	605
	R = $N(CH_2)_4$	**2b**	-7.69	611
		**2c**	-9.45	635
	R = OMe	**2d**	-12.18	424
	R = NMe_2	**2e**	-13.39	533
	R = 4-NO_2	**2f**	-14.36	374
	R = 3,5-F	**2g**	-14.50	350
	R = 4-OMe	**2h**	-16.11	393
		**2i**	-17.90	521

J. Zhang, Dr. J.-D. Yang, Prof. Dr. J.-P. Cheng
Center of Basic Molecular Science, Department of Chemistry,
Tsinghua University, Beijing 100084, China.
J.-D. Yang ORCID: 0000-0001-7351-2152
E-mail: jinpei_cheng@mail.tsinghua.edu.cn
jdyang@mail.tsinghua.edu.cn
Prof. Dr. J.-P. Cheng
State Key Laboratory of Elemento-organic Chemistry, College of
Chemistry, Nankai University, Tianjin 300071, China.
E-mail: chengjp@nankai.edu.cn
Supporting information for this article is given via a link at the end

10.1002/anie.201901456

Diazaphospholenes **1a-f** were prepared according to literature[2a, 3, 15] or our modified procedures (see Supporting Information, SI). Representative reaction outcomes can be found in Scheme 1 (for others, see SI). Benzhydrylium ion **2c** was observed to react with **1b-f** quantitatively in CH_3CN to furnish the corresponding diarylmethane. The reactions of quinone methide **2d** with **1d** and **1f** also gave the desired diarylmethane in fairly high yields. Similar results were obtained for the reactions of **2h** with **1a** and **1b**.



Scheme 1. Isolated yields for the reactions of **1** with reference electrophiles in CH_3CN. Details are shown in SI.

The kinetics of the reactions of **1a-f** with benzhydrylium ions **2a-c** or quinone methides **2d-i** was investigated by following the disappearance of the UV/Vis absorptions of the reference electrophiles under pseudo-first-order conditions ($[\mathbf{1}]_0/[\mathbf{2}]_0 > 10$), using stopped-flow spectrophotometer (Figure 2, for others see SI). The second-order rate constants k_2, *i.e.*, the slopes of the plots for the first-order rate constants k_{obs} vs the concentrations of nucleophiles **1**, are presented in Table 2. It is worth mentioning that **1b**, **1c** and **1e** reacted much more rapidly with **2i** than expected (see more details in the SI).

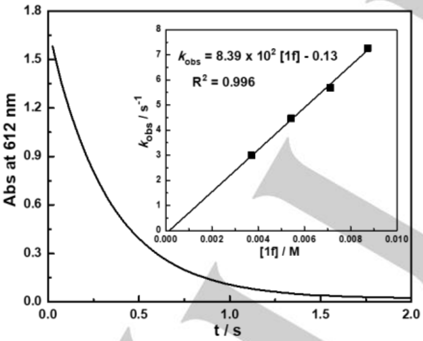
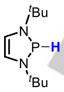
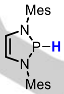
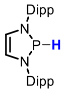
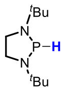
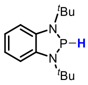
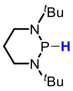


Figure 2. Monoexponential decay of the absorbance *Abs* (at 612 nm) with time for the reaction of **2b** (1.10×10^{-5} M) with **1f** (3.70×10^{-3} M) in CH_3CN at 20 °C. Inset: Correlation of k_{obs} with the concentrations of **1f**.

Plots of logk_2 vs E values (Table 1) for the reactions of **1** with electrophiles **2** were linear, allowing the nucleophile-specific sensitivity parameters (s_N) and the nucleophilic parameters (N) of hydrides **1** to be evaluated from the slopes and horizontal intercepts (Figure 3 and Table 2), respectively, by using eq. (1). As shown in Table 2, experimental rate constants k_2^{exp} agree well with the k_2^{calcd} predicted from eq. (1) using the E, N and s_N values in Tables 1 and 2, within a factor (k_2^{calcd}/k_2^{exp}) of 3 (note that factor < 100 is regarded a reasonable agreement[16]). The s_N values of hydrides **1** are generally in a range of 0.34 ~ 0.68, smaller than the previously reported values for C-H, B-H and Si-H hydride donors ($s_N > 0.6$).[17] In fact, such small s_N has only been previously found in extremely reactive nucleophilic systems,[16] suggesting an insensitivity (*i.e.*, low selectivity) of highly strong hydride donors to electrophiles. Nevertheless, **1b** gives a somewhat greater s_N (0.68), due most likely to a less steric repulsion of **1b** to benzhydrylium ion **2c** than to quinone methides. As a consequence, the hydride transfer from **1b** to **2c** should be faster. This leads to a larger slope of the fitted plot of logk_2 vs E for **1b** (Table S10). As for the reactions of **1c**, the very high congestion of its bulky Dipp groups makes it even less sensitive to distinguish the steric difference between benzhydrylium ions and quinone methides, resulting in a smallest s_N value.

Table 2. Second-order rate constants k_2 for the reactions of reagents **1** with reference electrophiles **2** in CH_3CN at 20 °C. Mes = 2,4,6-$Me_3C_6H_2$ and Dipp = 2,6-$^iPr_2C_6H_3$.

Nucleophiles	N (s_N)		k_2^{exp} (M^{-1} s^{-1})	k_2^{calcd}/k_2^{exp}
1a 	25.54 (0.35)	**2e**	$(1.57 \pm 0.06) \times 10^4$	1.13
		2f	$(8.70 \pm 0.19) \times 10^3$	0.94
		2h	$(1.95 \pm 0.06) \times 10^3$	1.03
		2i	$(4.40 \pm 0.13) \times 10^2$	1.07
1b 	17.68 (0.68)	**2c**	$(7.28 \pm 0.56) \times 10^5$	0.54
		2d	$(2.14 \pm 0.05) \times 10^3$	2.57
		2g	$(8.41 \pm 0.19) \times 10^1$	1.72
		2h	$(2.30 \pm 0.05) \times 10^1$	0.51
1c 	19.85 (0.34)	**2b**	$(1.25 \pm 0.05) \times 10^4$	1.09
		2c	$(3.08 \pm 0.17) \times 10^3$	1.11
		2d	$(3.69 \pm 0.02) \times 10^2$	1.10
1d 	18.74 (0.47)	**2c**	$(2.18 \pm 0.09) \times 10^4$	1.06
		2d	$(1.40 \pm 0.06) \times 10^3$	0.86
		2e	$(4.46 \pm 0.04) \times 10^2$	0.73
		2h	$(1.68 \pm 0.06) \times 10^1$	1.02
1e 	20.93 (0.43)	**2d**	$(6.21 \pm 0.20) \times 10^3$	0.93
		2g	$(5.55 \pm 0.18) \times 10^2$	1.05
		2h	$(1.30 \pm 0.05) \times 10^2$	0.91
1f 	13.46 (0.52)	**2a**	$(2.05 \pm 0.08) \times 10^3$	1.09
		2b	$(8.39 \pm 0.31) \times 10^2$	1.19
		2c	$(1.63 \pm 0.04) \times 10^2$	0.75
		2d	3.56 ± 0.17	1.30
		2e	1.04 ± 0.04	1.05

For the purpose of comparison, the nucleophilicity parameters N of P-H hydrides **1a-e** of this work, together with those of some conventional hydride donors, are drwan in Figure 4. The N value of the six-membered N-hetercyclic P-H compound **1f**[15] was also investigated in this work and included in Figure 4 for the same purpose. It can be seen from the right side of Figure 4 that the P-H centered N scale covers over ten N units, ranking as **1a** (25.5) >> **1b-e** (20.9-17.7) >> **1f** (13.5). Note that most of the P-H hydrides examined, except for **1f**, are much more reactive than those commonly used $NaBH_4$, dihydropyridines and metal hydrides, with **1a** ($N = 25.54$) as the most nucleophilic donor ever quantified by eq. (1). The super hydricity of **1a** was already confirmed by Gudat et al., who found that **1a** can directly transfer a hydride to aldehydes and diarylketones (within two minutes), and even to alkylketones (*E* = -22.30), although rather slowly.[3] The powerfulness of **1a** was also evidenced in other applications such as in catalytic reductions of imines,[5a] azocompounds,[7] pyridines[9a] and CO_2[8]. According to the nucleophilicity parameters disclosed here, **1a** should be roughly 10^2 times more reactive than **1d** (*N* = 18.74). This is obviously due to the aromaticity of the resulted **1a** phosphenium cation.

On the other hand, the aryl groups either on the N atom or in a benzannulated moiety, like in **1b**, **1c** and **1e**, appeared to attenuate the P-H nucleophilicity of the corresponding phospholenes compared to **1a** (*N* = 25.54), depressing their *N* values down to 17.68, 19.85, and 20.93, respectively**.** Indeed, it is convinced by the observed lower catalytic reactivity of **1b** than **1a** in imine reduction.[5a] As for the six-membered ring hydride **1f** (*N* = 13.46), it shows the least nucleophilicity in this series, which is close to that of $NaBH_4$ but still much more reactive than the renowned biomimetic and the metal hydrides depicted in Figure 4. These structure–reactivity analyses indicate that the incubated aromaticity should be the primary factor to the exceptional nucleophilicity of **1a**.

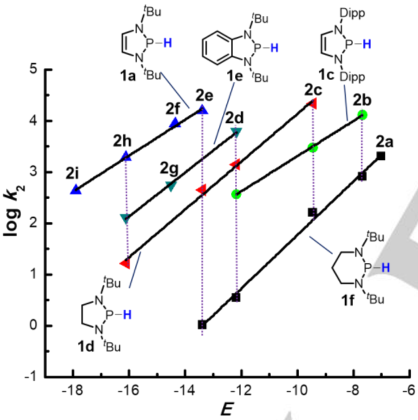


Figure 3. Plots of logk_2 for the reactions of reference electrophiles **2a**-**i** with **1a** and **1c**-**f** against the electrophilicity parameters *E* (see Table S10 for **1b**).

To apply the *N* parameters to examine the feasibility of a reaction, one can refer to a recent example specified for fluoromethylthiolating reagents.[11f] As showed therewith, a reaction system with *E* + *N* = -3, as estimated from eq. (1) assuming the sensitivity parameter s_N close to unity, can proceed in a rate around 10^{-3} M^{-1} s^{-1} at 20 °C. This value of -3 can be taken as an empirical criterion for judging whether or not a non-catalytic reaction can occur spontaneously at room temperature.[11f] However, in the present work, since the s_N values are in the range of 0.34 ~ 0.68, the original term in Mayr equation, *i.e.*, $s_N(E + N)$, instead of the simplified one *E* + *N*, should be used for predicting the rate constants. Rate constants between 10^{-2} ~ 10^{-1} M^{-1} s^{-1} can be expected for electrophiles and nucleophiles on the same level of Figure 4. Thus, one can expect that hydrides **1** will be able to react smoothly with a particular electrophile provided that the reaction can satisfy the criterion of *E* + *N* > -3. In other words, to expect a hydride-transfer reaction from P-H reagents to certain electrophiles to occur, one has to select the electrophile (see left side of Figure 4) with an *E* value that allows the sum of (*E* + *N*) to be larger than -3.

Due to their superior reactivity, all P-H hydrides investigated here would be expected to react readily with common oxidants (*e.g.*, trityl cation and DDQ) and iminium ions. This has been verified by the experiments demonstrated in Table 3, where three P-H reagents of different structural features (**1a**, **1d**, and **1f**) were allowed to react with representative electrophiles at 20 °C in CH_3CN. As predicted by eq. (1), the super-hydride **1a** can react with all electrophiles in Figure 4, including the extremely inert α,β-unsaturated esters **3e** and **3f** (*E* = -22.77 and -24.52), with quantitative conversion.

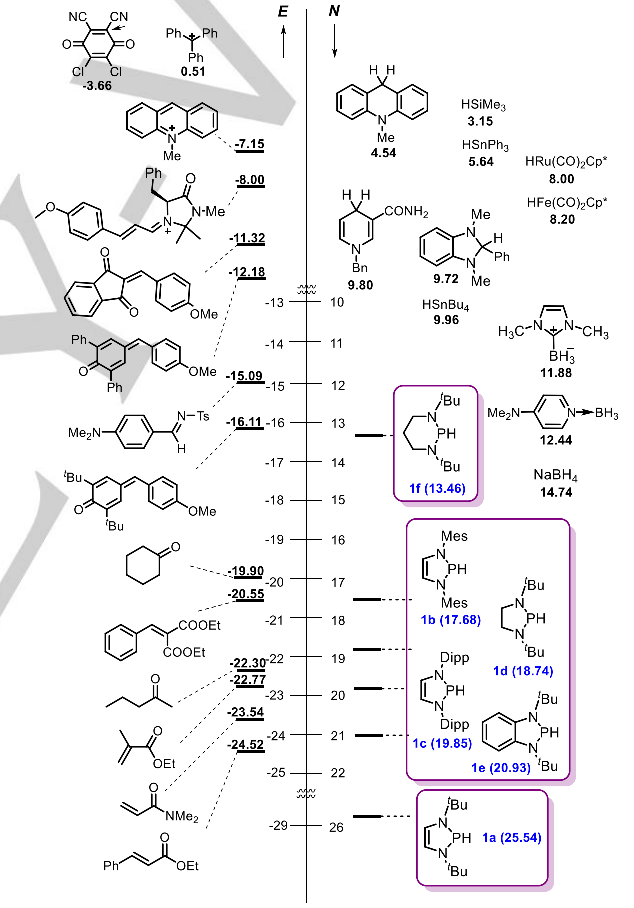
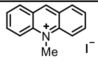
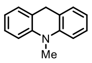
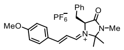
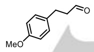
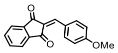
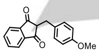
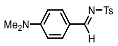
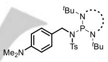
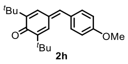
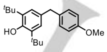
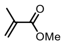
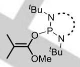
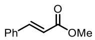
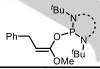


Figure 4. Comparision of nucleophilicity parameters *N* of **1a**-**f** with those of other hydride donors and predicting the scope of reactions of **1a**-**f** with carbon-centered electrophiles.[18]

As observed, the reactions of the relatively weak donor **1d** with α,β-unsaturated esters rendered a sluggish process with a yield less than 10% after 3 h, which is basically in accordance with the prediction based on eq. (1) [$s_N(N + E)$ = -1.93 for methyl methacrylate **3e**, and -2.72 for methyl cinnamate **3f**]. Table 3 also revealed that the electrophiles on a higher position in the left of Figure 4 (*e.g.*, N-methylacridinium **3a**, MacMillan-iminium **3b**, 2-benzylidene-indan-1,3-dione **3c**, active imine **3d,** and **2h**) could react smoothly with **1d** (yields > 80%). Also, as can be understood, the **1a** (N = 25.54) and **1b** (N = 17.68) P-H agents, which are generated *in-situ*, were reported to be able to catalyze the imine reduction by pinacolborane [HB(pin)] in 98% and 25% yields, respectively.[5a] The different performances of **1f** between the reactions with stronger electrophiles (such as iminium ions, active imines and quinone methides) and with less electrophilic α,β-unsaturated esters can be easily understood by following the same line of argument.

Surprisingly, the analogous reaction of **1d** derivative with a similar N value as **1b** (18.74 vs 17.68) was reported incapable. This discrepancy in catalytic performance could, however, not be simply viewed as a collapse of the above mentioned judging-rule. Instead, it may be used as a handy tool for probing other undetected factors at work in complex systems. Although attempts to untangle similar puzzles occasionally appeared in literature,[5a, 9a] more intensive research in future to identify the insights behind abnormal observations should be highly recommended.

Table 3. Reactions of P-H reagents **1a**, **1d** and **1f** with typical electrophiles in CH_3CN at 20 °C. Reaction conditions: **1** (0.2 mmol), nucleophiles (0.2 mmol), CH_3CN or CD_3CN (1 mL), 20 °C, 30 min.

Electrophile	E	**1a**	**1d**	**1f**	Product
 **3a**	-7.15	>90%[a]	>90%[a]	>90%[a]	
 **3b**	-8.00	90%[b]	92%[b]	87%[b]	
 **3c**	-11.32	+[c]	81%[b]	87%[b]	
 **3d**	-15.09	+[c]	>90%[a]	55%[a,f]	
 **2h**	-16.11	88%[b]	87%[b]	70%[a,f]	
 **3e**	-22.77[g]	Quant.[d]	<10%[a,e,f]	0	
 **3f**	-24.52[g]	>90%[a]	<10%[a,e,f]	0	

[a] Yields were determined by ^1H NMR analysis using CH_2Br_2 as the internal standard. [b] Isolated yields. [c] Reactions expected, but not tested. [d] From reference 5b. [e] With some unidentified side products. [f] Reaction time: 3 h. [g] Estimated values from similar structures in Figure 4.

Besides the product analyses, kinetic examinations (k_2) of the reactions of diazaphospholenes **1** with several electrophiles **3** (Table S36) were also performed, which appeared to match the values predicted by eq. (1).

In summary, the first P-H type nucleophilicity scale in terms of the Mayr's N and s_N values for the diazaphospholenium ions **1** was established to be in an N range of 13.5 ~ 25.5, with N of 25.5 for **1a** as the most nucleophilic hydride donor ever quantified by the Mayr equation. Successful applications of the empirical criterion of $E + N > -3$ verified the good value of these parameters in rationalizing experimental observations and predicting feasibility of reactions, adding confidence for their use as a guiding index in the development of new diazaphospholenium-like reagents and the relevant transformations.

Acknowledgements

We are grateful for the financial grants from National Natural Science Foundation of China (Nos. 21672124, 21602116, 21772098, 91745101), and Tsinghua University Initiative Scientific Research Program (Nos. 20131080083, 20141081295).

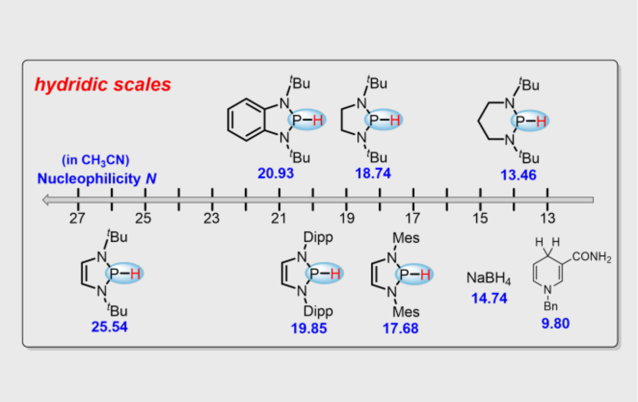
Keywords: P-H hydride • diazaphospholene • nucleophilicity parameter • linear free-energy relationship • structure–reactivity relationship

[1] (a) Z. Xu, P. Wang, Q. Chen, M. Cai, *J. Organomet. Chem.* **2018**, *866*, 50-58; (b) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, V. P. Wystrach, *J. Am. Chem. Soc.* **1959**, *81*, 1103-1107; (c) A. D. Sadow, A. Togni, *J. Am. Chem. Soc.* **2005**, *127*, 17012-17024; (d) Y. Moglie, M. J. González-Soria, I. Martín-García, G. Radivoy, F. Alonso, *Green Chem.* **2016**, *18*, 4896-4907.
[2] (a) D. Gudat, A. Haghverdi, M. Nieger, *Angew. Chem. Int. Ed.* **2000**, *39*, 3084-3086; (b) D. Herrmannsdörfer, M. Kaaz, O. Puntigam, J. Bender, M. Nieger, D. Gudat, *Eur. J. Inorg. Chem.* **2015**, *2015*, 4819-4828; (c) D. Gudat, *Dalton Trans.* **2016**, *45*, 5896-5907; (d) D. Gudat, *Acc. Chem. Res.* **2010**, *43*, 1307-1316.
[3] S. Burck, D. Gudat, M. Nieger, W.-W. Du Mont, *J. Am. Chem. Soc.* **2006**, *128*, 3946-3955.
[4] S. Ilic, A. Alherz, C. B. Musgrave, K. D. Glusac, *Chem. Soc. Rev.* **2018**, *47*, 2809-2836.
[5] (a) M. R. Adams, C. H. Tien, B. S. N. Huchenski, M. J. Ferguson, A. W. H. Speed, *Angew. Chem. Int. Ed.* **2017**, *56*, 6268-6271; (b) C. C. Chong, B. Rao, R. Kinjo, *Acs. Catal.* **2017**, *7*, 5814-5819.
[6] C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2015**, *54*, 190-194.
[7] C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3342-3346.
[8] C. C. Chong, R. Kinjo, *Angew. Chem. Int. Ed.* **2015**, *54*, 12116-12120.
[9] (a) B. Rao, C. C. Chong, R. Kinjo, *J. Am. Chem. Soc.* **2018**, *140*, 652-656; (b) T. Hynes, E. N. Welsh, R. McDonald, M. J. Ferguson, A. W. H. Speed, *Organometallics* **2018**, *37*, 841-844.
[10] (a) M. R. Adams, C.-H. Tien, R. McDonald, A. W. H. Speed, *Angew. Chem. Int. Ed.* **2017**, *56*, 16660-16663; (b) S. Miaskiewicz, J. H. Reed, P. A. Donets, C. C. Oliveira, N. Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 4039-4042.
[11] (a) X.-Q. Zhu, Y. Tan, C.-T. Cao, *J. Phys. Chem. B* **2010**, *114*, 2058-2075; (b) D. Richter, Y. Tan, A. Antipova, X.-Q. Zhu, H. Mayr, *Chem. Asian J.* **2009**, *4*, 1824-1829; (c) X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501-2516; (d) X.-Q. Zhu, Y. Yang, M. Zhang, J.-P. Cheng, *J. Am. Chem. Soc.* **2003**, *125*, 15298-15299; (e) J.-D. Yang, B.-L. Chen, X.-Q. Zhu, *J. Phys. Chem. B* **2018**, *122*, 6888-6898; (f) J. Zhang, J. D. Yang, H. Zheng, X. S. Xue, H. Mayr, J. P. Cheng, *Angew. Chem. Int. Ed.* **2018**, *57*, 12690-12695; (g) Internet Bond-energy Databank (iBonD) Home Page: http://ibond.nankai.edu.cn or http://ibond.chem.tsinghua.edu.cn.
[12] H. Mayr, M. Patz, *Angew. Chem. Int. Ed.* **1994**, *33*, 938-957.
[13] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500-9512.
[14] (a) R. Lucius, R. Loos, H. Mayr, *Angew. Chem. Int. Ed.* **2002**, *41*, 91-95; (b) D. Richter, N. Hampel, T. Singer, A. R. Ofial, H. Mayr, *Eur. J. Org. Chem.* **2009**, *2009*, 3203-3211.
[15] R. B. King, P. M. Sundaram, *J. Org. Chem.* **1984**, *49*, 1784-1789.
[16] (a) B. Maji, M. Breugst, H. Mayr, *Angew. Chem. Int. Ed.* **2011**, *50*, 6915-6919; (b) O. Kaumanns, R. Appel, T. Lemek, F. Seeliger, H. Mayr, *J. Org. Chem.* **2009**, *74*, 75-81; (c) Z. Li, Q. Chen, P. Mayer, H. Mayr, *J. Org. Chem.* **2017**, *82*, 2011-2017; (d) D. S. Allgäuer, P. Mayer, H. Mayr, *J. Am. Chem. Soc.* **2013**, *135*, 15216-15224.
[17] (a) M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr, A. R. Ofial, *Chem. Eur. J.* **2013**, *19*, 249-263; (b) H. Mayr, G. Lang, A. R. Ofial, *J. Am. Chem. Soc.* **2002**, *124*, 4076-4083; (c) V. Morozova, P. Mayer, G. Berionni, *Angew. Chem. Int. Ed.* **2015**, *54*, 14508-14512.
[18] For a comprehensive database of electrophilicity parameters E and nucleophilicity parameters N and s_N, see: http://www.cup.lmu.de/oc/mayr/DBintro.html.

Entry for the Table of Contents

Layout 2:

COMMUNICATION



Jingjing Zhang, Jin-Dong Yang, Jin-Pei Cheng**

Page No. – Page No.

Nucleophilicity Scale for the Reactivity of Diazaphospholenium Hydrides: Structural Insights and Synthetic Applications

P-H super-hydrides: The unexpected philicity of P-H bonds in diazaphospholenes has made their applications to catalytic reductions a burgeoning field. Herein, we used a three-parameter kinetic equation to evaluate their nucleophilicity parameters (*N*), which cover over ten *N* units. Kinetic studies imply their much superior hydricity over commonly-used hydrides, with 2-*H*-1,3,2-diazaphospholene being the strongest nucleophilic donor ever quantified by Mayr equation. These reactivity parameters are beneficial to the rational design of diazaphospholene-involved reactions.