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Influence of *N*-Heterocyclic Carbenes (NHCs) on the Hydrolysis of a Diphosphene

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We report the influence of N-heterocyclic carbenes (NHCs) on the hydrolysis of a diphosphene TerP=PTer (1; Ter = 2,6-Mes₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂), a phosphorus-analogue of an alkene. The diphosphene 1 itself is completely inert towards water. However, NHCs have been found to activate 1 towards ready hydrolysis. While sterically less-encumbered NHCs react with 1 affording NHC-adducts which are in equilibrium with 1 in solution, sterically encumbered NHCs do not bind to 1 at all. Interestingly, in both of these situations hydrolysis of the P=P motif proceeds efficiently. At low temperatures, sterically less-encumbered NHCs are catalytic while the sterically encumbered NHCs play a catalytic role at room temperature. To gain insight on this striking influence of NHCs on the hydrolysis of diphosphene detailed lowtemperature ³¹P-NMR studies along with theoretical calculations have been carried out. In addition, systematic hydrolysis studies of all the NHCs used in this study have also been performed.

N-heterocyclic carbenes (NHCs)¹ play an important catalytic role in various organic transformations involving transition metal catalysis² as well as organocatalytic reactions.³ Although the strong σ -donating ability of NHCs is their forte,⁴ the reversible binding of NHCs with organic substrates in organocatalytic reactions is one of the important features responsible for their catalytic role in organic transformations.⁵ The reversible binding of NHCs with compounds involving 3rd row main-group elements is known,⁶ but their catalytic involvement in such reactions was unknown until our report on the reactivity enhancement of a diphosphene, TerP=PTer (**1**; Ter = 2,6-Mes₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂) by the reversible

^{b.} New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India, E-mail: pati@jncasr.ac.in coordination of **NHC^{Me}4** towards hydrolysis as well as hydrogenation with **NH₃·BH**₃.⁷ A perusal of the literature has revealed a striking influence of the nature of NHCs on the reaction outcome.⁸



Scheme 1. Chemical structures of NHCs used in this study.

These factors have spurred us to undertake a detailed study on the influence of different electronically and sterically modified *N*-heterocyclic carbenes (NHCs)⁹ (Scheme 1) on the hydrolysis of a diphosphene which is otherwise inert towards water. We were also keen to examine if the NHCs had any catalytic role in the hydrolysis reaction of the olefin analogue. First, we considered the reversible binding properties of various NHCs with the diphosphene and then examined the hydrolysis reaction both in presence of stoichiometric as well as catalytic amounts of NHCs. Variable temperature (VT) ³¹P-NMR was used extensively along with theoretical calculations to understand the nuances of the progress of the reaction. We also studied the hydrolysis of all the NHCs used in the current investigation to throw light on their role in the hydrolysis of the diphosphene.



 $\mathsf{NHC}^{\mathsf{R'R''R_2}}=\mathsf{NHC}^{\mathsf{Me_4}},\ \mathsf{NHC}^{\mathsf{iPr_2Me_2}},\ \mathsf{NHC}^{\mathsf{Me_2}},\ \mathsf{NHC}^{\prime\mathsf{PrMe_3}}$

Scheme 2. Reaction of 1 with NHCs under the reversible formation of 1-NHC^{R'R''R}2.

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Room temperature solution state ³¹P NMR studies revealed that $\rm NHC^{Me_2}$ binds with 1 and forms about 20% of $\rm 1{\cdot}NHC^{Me_2}$ (Scheme 2).¹⁰ On the other hand, with NHCMe4 70% adduct formation is observed under similar conditions.⁷ This observation suggests that NHCMe4 is more nucleophilic than NHC^{Me2}, which is in accordance with the calculated Tolman electronic parameters (TEP) ($v(cm^{-1}) = 2051.7$ for **NHC^{Me4}** and 2054.1 for NHCMe2).11 The other NHCs that we employed did not show any adduct formation at rt, presumably because of their lower nucleophilicity arising from increased steric bulk. As entropy should favor adduct formation at lower temperature, VT ³¹P NMR of the corresponding mixtures of NHCs with 1 expectedly revealed first indications of 1.NHC^{iPrMe} at 273 K, whereas the observation of 1.NHC^{/Pr2} required a temp as low as 233 K (Scheme 2). Conversely, NHC^{iPr2Me2}, NHC^{tBu2}, NHC^{Dip2} and NHC^{Mes2} do not appear to be involved in adduct formation even at 193 K.

From the ³¹P NMR spectra, the formation of 1.NHC^{Me2} and 1-NHC^{iPr2} is indicated by the presence of two doublets while just one singlet is observed for the diphosphene, 1. In the case of NHC^{/PrMe}, the differing N-substitution in concert with hindered rotation about the P-C bond between the carbenic carbon and phosphorus leads to the formation of diastereomers. The ³¹P NMR spectrum of 1·NHC^{iPrMe} shows two sets of doublets centred at 19.1 and -87.6 ppm (${}^{1}J_{PP} = 405$ Hz) and 1.1 and -92.6 ppm (${}^{1}J_{PP}$ = 430 Hz), the latter being the major isomer. In order to quantify the thermodynamic parameters (Δ G, Δ H, and Δ S) and equilibrium constants of the binding of NHCMe2, NHCiPrMe and NHCiPr2 with 1, we have recorded VT-³¹P NMR spectra of the corresponding 1:1 mixture in toluene-d₈ solutions.¹⁰ The obtained ΔG_{298} for **NHC^{Me2}** is -3.6 ± 1.3 kJ/mol which is less negative than that of NHC^{Me4} $(\Delta G_{298} = -11.2 \pm 1.1 \text{ kJ/mol}).^7$ This clearly indicates that **NHC**^{Me2} is a weaker donor than NHCMe4. On the other hand, the obtained ΔG_{298} for NHC^{iPrMe} and NHC^{iPr2} is +5.8 ± 3.51 and +20.9 ± 7.81 kJ/mol, respectively. Bright red single crystals of 1-NHC^{Me2} were obtained from a saturated toluene solution at -35 °C along with 1. Which allowed selectively to recorded the solid state molecular structure of 1.NHC^{Me2} (Figure 1).



Figure 1 Molecular structures of 1-NHC^{Me2} in the solid state with thermal ellipsoids at 50%.

The bonding properties of the NHC-coordinated diphosphenes **1**·**NHC**^{Me}², **1**·**NHC**^{*i*Pr}² and **1**·**NHC**^{*i*PrMe} were examined by DFT calculations employing the B3LYP-D3

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exchange-correlation functional.¹⁰ The NHC-coordination results in the elongation in the P-PO:bond39length4Gand accordingly, the WBI values in the NHC-coordinated diphosphenes are significantly lower (between 1.13-1.15) compared to **1**. The HOMO is mainly composed of a *p*-orbital at the non-NHC coordinated P-center confirming the presence of the nonbonding lone pair. The LUMO is more delocalized and distributed over the NHC and phenyl-moieties on the NHCcoordinated P-center.¹⁰ Compound **1** readily reacts with water in THF in the presence of **NHC**^{Me}₄ to afford phosphinophosphine oxide, **3** (5%) and phosphido oxide, **4-NHC**^{Me}₄ (95%) (Scheme 3).⁷



Scheme 3. Stoichiometric reaction of H₂O with mixture of 1 and NHC^{Me₄}.

The reaction is catalytic with respect to the NHC^{Me4} at -78 °C (195 K). These observations leave several unanswered questions regarding the role of $\mathbf{NHC}^{\mathbf{Me_4}}$ and the collapse of the catalytic cycle at higher temperatures. Notably, NHCMe4 itself is sensitive to hydrolysis (vide infra). Under these circumstances, how does NHC^{Me4} promote the hydrolysis reaction of 1? In order to gain some insight into these queries, we studied the reaction mixture of 1 and NHCMe4 in the presence of stoichiometric amount of water at low temperature by measuring the $^{\rm 31}{\rm P}$ NMR spectra. As the temperatures are increased from 193 K to 263-273 K, two resonances are observed at 111.0 (d) and -34.2 (dd) ppm with ${}^{1}J_{PP}$ = 338 Hz and ${}^{1}J_{HP}$ = 209 Hz in the ${}^{31}P$ NMR spectrum. We attribute these signals to the 1,2-addition of water to a diphosphene under formation of **2-NHC^{Me4}** with a P-H moiety (Scheme 3). The formation of a 1,1-addition product can be safely ruled out as it is determined to be 102.9 kJmol⁻¹ less stable (on the basis of electronic energy) than the 1,2-addition product by DFT calculation.¹⁰ Clearly, such an initial water addition product,

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2-NHC^{Me}₄, is not stable at room temp (and even at 273 K) and thus it leads to the formation of **3** and **4-NHC^{Me}**₄. To get doubly hydrolyzed product as known in case of the heteroleptic diphosphene¹² we have carried out the reaction of **1** with 2 equiv of **H**₂**O** and 2 equiv of **NHC^{Me}**₄ in THF. However, this reaction also leads to the same results as obtained with one equivalent of H₂O and NHC.¹⁰

Since the NHCs, **NHC^{Me}2**, **NHC**^{*i*PrMe}, and **NHC**^{*i*Pr2} were found to bind with **1**, as shown above, we investigated the reaction of **1** with water after stoichiometric addition of these NHCs. These reactions resulted in the formation of **3** along with the corresponding zwitterionic compounds **4**·**NHC**^{*Me*}**2**, **4**·**NHC**^{*i*PrMe} and **4**·**NHC**^{*i*Pr2}, respectively. Analysis of the single crystal X-ray data of **4**·**NHC**^{*i*PrMe} confirms its formation (Figure S54 in ESI).¹⁰ Instead of stoichiometric amounts of the NHCs, we then attempted the catalytic hydrolysis of **1** in the presence of 10 mol % of **NHC**^{*Me*}**2**, **NHC**^{*i*PrMe}, and **NHC**^{*i*Pr2} (Scheme S1 in ESI). Under these conditions, predominantly **3** is formed and found alongside unreacted diphosphene, **1**. In order to improve the yield, the addition of water has to be carried out in portions to avoid hydrolysis of the corresponding NHC, which arrests the catalytic turnover.

While NHC^{/Pr2Me2}, NHC^{tBu2}, NHC^{Dip2}, and NHC^{Mes2} do not form an adduct with 1, we wished to examine their role in assisting the hydrolysis of it. We hypothesized that while actual adduct formation might not occur, these NHCs in proximity to the P=P might polarize it towards further reactivity. Indeed, the reaction of 1 and H_2O in presence of a stoichiometric amount of NHC^{iPr2Me2} in THF seems to go to completion; the ³¹P NMR shows complete consumption of the starting diphosphene and formation of a new compound $2{\cdot}NHC^{\textit{i}Pr_2Me_2}$ (90 %) as the major product alongside 3 and 4.NHC^{/Pr2Me2} (Scheme 4). Efforts to isolate 2.NHC^{/Pr2Me2} resulted invariably in the isolation of 4.NHCMe2iPr2 (90%) along with 7% of 3 and 3% of 2·NHC^{iPr2Me2}. To further probe this reaction, we investigated the low-temperature ³¹P NMR of the reaction mixture. At 203 K two doublets of doublets at 123.1 (${}^{1}J_{P,P}$ = 308 Hz, ${}^{2}J_{PH}$ = 18 Hz) and -47.8 (${}^{1}J_{PP}$ = 308 Hz, ${}^{1}J_{PH}$ = 222 Hz) ppm are observed, which are indicative of the formation of the water addition product 2·NHC^{/Pr2Me2}. After two days we see the conversion to 3 and 4.NHC^{/Pr2Me2} with only a small amount of 2.NHC^{/Pr2Me2} remaining. The ¹H NMR spectrum confirms the involvement of NHC^{iPr2Me2} in 2·NHC^{iPr2Me2}. The pattern and trends of ³¹P chemical shifts as well as the coupling constants of the initial addition product 2.NHC^{iPr2Me2} are similar to those of $2 \cdot NHC^{Me_4}$ (Scheme 3). The structural assignment is further supported by the addition of NHCMe4 to a solution of 2.NHC^{iPr₂Me₂, which immediately results in its conversion to 3} and 4.NHC^{Me4}. Treatment of 2.NHC^{iPr2Me2} with the Lewis acid BPh₃ as an NHC scavenger¹³ results in the formation of 2 immediately; which slowly rearranges to compound 3 in 24 hrs. Due to the hindered rotation about the P-P bond. 2 occurs as two conformational isomers in a 7:10 ratio with one set of doublet of doublets in the ³¹P NMR spectrum. Compound 2 formally constitutes a 1,2-addition product of water to a diphosphene, which in analogy to phosphinous acids R₂POH tautomerizes to the corresponding phosphorus oxide



Scheme 4. Stoichiometric reaction of H₂O with mixture of 1 and NHC^{iPr₂Me₂.}

Despite the comparatively high stability of the alleged intermediate **2·NHC^{***i***Pr₂Me₂, we considered the use catalytic amounts of NHC^{***i***Pr₂Me₂** (10 mol%) in THF for the hydrolysis of **1**. At low temperature (–78 °C), indeed no catalytic activity is seen (Scheme 4). At rt, however, the reaction affords **3** almost quantitatively (95%) alongside about 2.5% of **4·NHC^{***i***Pr₂Me₂**. Although we do not observe **2·NHC^{***i***Pr₂Me₂** in the catalytic reaction, it must be involved as an intermediate, which quickly releases the **NHC^{***i***Pr₂Me₂ to regenerate 2·NHC^{***i***Pr₂Me₂** (Scheme S2 in ESI). Analysis of the single crystal X-ray data of **4·NHC^{***i***Pr₂Me₂** shows its formation (Figure 2).}}}}}}}



Figure 2. Molecular structures of $4\cdot NHC^{iPr_2Me_2}$ in the solid state with thermal ellipsoids at 50%.

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With NHC^{rBu}² in THF we observe the direct formation of **3**, in almost 90% spectroscopic yield, along with 5% of **4**·NHC^{rBu}² and 5% of **2**·NHC^{rBu}².¹⁰ Catalytic use of NHC^{rBu}² also leads quantitatively to the formation of **3**. On the other hand with NHC^{Dip}² we observe the formation of **3** (20%) along with unreacted diphosphene, **1** (80%), even after two days. With NHC^{Mes}², **1** remains unchanged in reaction with one equivalent of water even after 5 days.

The fact that **NHC**^{*i*Pr₂Me₂} does not catalyze the reaction at low temperatures while **NHC**^{Me₄} does, raised the question if the reactivity of the NHCs with water itself might be detrimental to the catalytic turnover. We therefore investigated the hydrolysis reactions of all these NHCs in THF (Scheme 5).¹⁰ To our surprise, we found that the hydrolysis of **NHC**^{*i*Pr₂Me₂} with respect to **NHC**^{Me₄} is very slow; even after one month the reaction is not complete (Table 1). Therefore, **NHC**^{*i*Pr₂Me₂ can catalyze the reaction at rt. In order to correlate the relative basicity of the NHCs with their propensity towards hydrolysis, we have estimated their proton affinities (PAs) in the gas-phase via the Gibbs free energies for the proton detachment (PDFE) which supports our experimental findings.¹⁰}



Scheme 5. Hydrolysis reactions of NHCs.

Table 1. Reaction of different *N*-heterocyclic carbenes (NHCs) with H₂O.

SI No.	NHC ^{R'R''R} 2	Conversion of NHC ^{R'R''R} 2 (%) / Reaction Time at RT ¹⁰	Ratio of A and B	Reference
1	NHC ^{Me4}	100 / 1 hr	60:40	In this study
2	NHC ^{iPr} 2 ^{Me} 2	60 / 1 month	46:54	In this study
3	NHC ^{Me} 2	100 / 1 hr	Not able to assigned the ¹ H NMR spectrum	In this study
4	NHC ^{iPrMe}	100 / 1 hr	Not able to assigned the ¹ H NMR spectrum	In this study
5	NHC ^{iPr} 2	100 / 1 hr	100:0	15a
6	NHC ^{tBu} 2	< 1 / 5 days	0:100	15a
7	NHC ^{Dip} 2	57 / 10 days	25:75	15b
8	NHC ^{Mes} 2	95 / 5 days	60:40	15a

In conclusion, we report the influence of different NHCs on the reaction of water to a diphosphene. The sterically less encumbered and more basic NHCs bind to the diphosphene and thus afford adducts, which are in equilibrium with the diphosphene in solution. The other type of NHCs are sterically encumbered, less basic and do not bind to the diphosphene. However, in both cases the presence of NHCs induces

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hydrolysis of the diphosphene. In the latter case, we speculate that the close proximity of NHC and diphosphere? induced polarization of the P=P and hence the NHCs are able to catalyze the hydrolysis reaction. The enhancement of reactivity of the diphosphene is catalytic vis-à-vis the carbene. Thus, NHC^{Me4}, NHC^{Me2}, NHC^{/Pr2}, NHC^{/PrMe} are catalytic at low temperature while NHC^{iPr2Me2}, NHC^{tBu2} are catalytic at rt. Hydrolysis reactions of the native NHCs revealed that while the sterically unhindered carbenes hydrolyze instantly at rt, the bulkier carbenes hydrolyze more slowly, providing a straightforward explanation for the differing conditions necessary for the catalytic turnover. In addition, the NHCs used in this study are those that are commonly used by a broad-range of chemists. The systematic comparative hydrolysis study of these NHCs will be important in their choice as reagents/catalysts.

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Conflicts of interest

There are no conflicts to declare.

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Irrespective of reversible coordination or non-coordination of NHC to the diphosphene; the presence of it in a stoichiometric or even in catalytic leads to the hydrolysis of diphosphene.

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