Formylation or methylation: what determines the chemoselectivity of the reaction of amine, CO₂, and hydrosilane catalyzed by 1,3,2-diazaphospholene?†

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DFT computations have been performed to gain insight into the mechanisms of formylation/methylation of amines (e.g. methylaniline (1a)/2,2,4,4-tetramethylpiperidine (2a) with CO₂ and hydrosilane ([Si]H₂, [Si] = Ph₂Si), catalyzed by 1,3,2-diazaphospholene ([NHP]H). Different from the generally proposed sequential mechanism for the methylation of amine with CO₂, i.e. methylation proceeds via formylation, followed by further reduction of formamide to give an N-methylated amine, the study characterized a competition mechanism between formylation and methylation. The chemoselectivity originates from the competition between the amine and [NHP]H hydride to attack the formyloxy carbon of [Si](OCHO)₂ (the insertion product of CO₂ into [Si]H₂). When the attack of an amine (e.g. 1a) wins, the transformation affords formamide (1b) but would otherwise (e.g. 2a) result in an N-methylated amine (2c). The reduction of formamide by [Si]H₂ or [NHP]H is highly unfavorable kinetically, thus we call attention to the sequential mechanism for understanding the methylation of amine with CO₂. In addition, the study has the following key mechanistic findings. The activation of CO₂ by [NHP]H establishes an equilibrium: [NHP]H + CO₂ ⇌ [NHP]OCHO ⇌ [NHP]⁺ + HCO₂⁻. The ions play catalytic roles to promote formylation via HCO₂⁻ or methylation via [NHP]⁺. In 1a formylation, HCO₂⁻ initiates the reaction, giving 1b and silanol byproducts. However, after the initiation, the silanol byproducts acting as hydrogen transfer shuttles are more effective than HCO₂⁻ to promote formylation. In 2a methylation, [NHP]⁺ promotes the generation of the key species, formaldehyde and a carbocation species (IM17⁺). Our experimental study corroborates our computed mechanisms.

1. Introduction

The rising concentration of carbon dioxide (CO₂) in the atmosphere is one of the key factors for global warming, leading to great efforts to develop effective catalytic routes that convert CO₂ to value-added chemicals.¹⁻¹² Formylation and methylation of amines with CO₂ are promising synthetic strategies to use CO₂ as a C1 carbon source.⁴ In 1998, Vaska and coworkers developed the first Pt-catalyzed formylation of amine with CO₂ and H₂.⁵ This study has encouraged further developments using other transition metal catalysts⁶ or metal-free catalysts.⁷ In 2012, Cantat and coworkers achieved the first organocatalytic formylation of amines with CO₂ and hydrosilane, catalyzed by triazabicyclodecene (TBD).⁸ Since then, more similar transformations were reported.⁹ In 2013, Beller and coworkers reported the first methylation of amine with CO₂ and hydrosilane, catalyzed by a ruthenium complex.¹⁰ More similar transformations were later developed.¹¹ It is worth mentioning that Cantat et al. also developed metal-free methylation of CO₂ with amines.¹² Furthermore, transition metal catalyzed methylation of amines with CO₂ and H₂ has also been accomplished by several groups.¹³

Previously, we studied the catalytic mechanisms of CO₂ reduction to methanol¹⁴ and methane.¹⁵ In this context, we were intrigued by the catalytic reactions developed by Kinjo and coworkers.¹⁶ They used 1,3,2-diazaphospholene ([NHP]H) to catalyze the formylation of amines ([N]H) with CO₂ and hydrosilane (Ph₃SiH₂ = [Si]H₂) (e.g. eqn (1) in Scheme 1). Interestingly, two amines (2a and 3a) were found to be exceptional, affording N-methylated amines (2c and 3c). They attributed 2c and 3c to the further reductions of 2b and 3b, respectively, complying with the general consideration that methylation takes place sequentially through formylation, giving formamide, followed by the reduction of formamide.¹⁰,¹⁷ Nevertheless, we conceived that this mechanism may not be true in the

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Scheme 1 (A) Formylation (eqn (1)) and methylation (eqn (2) and (3)) of amines with CO2 and hydrosilane ([SiH2 = Ph2SiH3]), reported by Kinjo et al. (B) Schematic illustration of our proposed mechanism.

2. Computational details

Experimentally, the reactions were carried out in a polar solvent (acetonitrile, $\varepsilon = 35.7$). Considering the possible significant effects of the strong polar solvent, all geometries were optimized and characterized as minima (no imaginary frequency) or transition states (TSs, having one unique imaginary frequency) at the M06-2X/6-31G(d,p) level with the solvation effect of acetonitrile simulated by the SMD solvent model. At the M06-2X/6-31G(d,p) geometries, the energies were further refined by M06-2X/6-311+G(d,p) single-point energy calculations with the solvent effect accounted for by the SMD solvent model. All DFT calculations adopted ultrafine integration grids (Int = ultrafine) to ensure stable numerical integrations. The M06-2X/6-31G(d,p) frequencies were used for thermal and entropic corrections at 298.15 K and 1 atm. It should be emphasized that such a correction approach is based on the ideal gas phase model, which inevitably overestimates entropy contributions to free energies for reactions in solvent, in particular for reactions involving a multicomponent change, because they ignore the suppressing effect of solvent on the rotational and translational freedoms of substrates. The entropy overestimation of the approach was also demonstrated experimentally.22,23 While no standard quantum mechanics-based method is available to accurately calculate entropy in solution, approximate methods were proposed. According to the proposal of Martin et al.,24 we previously applied a correction of $(n - m) \times 4.3$ kcal mol$^{-1}$ for a process from m- to n-components and found that such corrected free energies were more reasonable than enthalpies and uncorrected free energies,15,25 although the protocol is by no means accurate. Other correction factors (e.g. 1.9,26 2.6,3a,27 and 5.4 kcal mol$^{-1}$ (ref. 28)) were adopted in the literature depending on the approximate approaches. As will be seen, our studied reactions involve multicomponent changes. As a conservative consideration, we applied a correction factor of
3. Results and discussion

In this study, we use eqn (1) as a representative to compute the formylation mechanism of amine 1a (Section 3.1). In Section 3.2, using eqn (2), we investigate the methylation mechanism of amine (2a). After characterizing the mechanisms of formylation and methylation, we discuss the origins of chemoselectivity and experimentally verify our proposed mechanism in Section 3.3. Our computed mechanisms involve ionic species, thus we explicitly label the charges of all species when applicable for simplicity of the descriptions.

3.1 Mechanism for 1a formylation (eqn (1))

The catalytic cycle for 1a formylation (eqn (1)) consists of three stages, namely, hydrophosphination of CO$_2$ (stage I), formation of diformyloxysilane (stage II), and C–N bond formation (stage III). We below characterize how these stages proceed in order.

Hydrophosphination of CO$_2$ (stage I). Fig. 1 illustrates the mechanism for CO$_2$ hydrophosphination, along with the key optimized structures. The catalyst [NHP]H is a hydride with P and H bearing 0.921 and $-0.069 e$ partial charges, respectively.

Conventionally, CO$_2$ prefers inserting into an E–H bond (e.g. E = B or Ni) via a four-membered TS, forming C–H and E–O bonds concerted.$^{14,15}$ However, the optimized structure of TS$_1$ targeting for an insertion TS describes a hydrogen abstraction process. Zhu et al. reported a similar TS.$^{31}$ The IRC (intrinsic reaction coordinate) calculation toward the product stopped after 129 steps (Fig. S1†), giving a structure (namely, IRCF-129) which can be viewed as an ion pair resulting from CO$_2$ abstraction of the H$^+$ atom of [NHP]H. However, geometric optimization starting from IRCF-129 reached an insertion product [NHP]OCHO (IM1). We attribute the abnormal insertion to the difference between the P$^+$–H$^+$ bond in [NHP]H and E$^+$–H$^+$ bond (e.g. B–H or Ni–H)$^{14,15}$ the P center has a lone pair disfavoring P–O bond formation, while the E center features an empty orbital favoring E–O bond formation. IM1 is different from the X-ray structure of the CO$_2$ hydrophosphination product [IM3] but can convert to the more stable IM3 easily (see Fig. 1). Overall, the insertion crosses a barrier of 16.7 kcal mol$^{-1}$ and is exergonic by 6.9 kcal mol$^{-1}$, indicating the feasibility of the process.

Kinjo et al. observed zwitterionic character of IM3. Consistently, the [NHP] and HCO$_2$ moieties in IM3 bear charges of 0.658 and $-0.658 e$, respectively. Because of the zwitterionic nature, we conceived that IM3 can dissociate easily in the strong polar acetonitrile solvent, as demonstrated by the small dissociation energy (4.6 kcal mol$^{-1}$, see Scheme 2). Thus a microscopic equilibrium is expected in this catalytic system. As will be shown, the free [NHP]$^+$ and HCO$_2^-$ ions play catalytic roles to mediate subsequent steps of the transformation.

Formation of diformyloxysilane[Si](OCHO)$_2$ (stage II). Experimentally, it has been demonstrated that [Si](OCHO)$_2$ is
involved in the transformation. Fig. 2 illustrates the possible pathways leading to [Si](OCHO)$_2$, along with the key optimized structures. The black pathway from IM3 to H[Si]OCHO in

Fig. 2 can be considered as a stepwise $\sigma$-bond metathesis between IM3 and [Si]H$_2$, which forms Si–O and P–H bonds and meanwhile breaks Si–H and P–O bonds, leading to H[Si]OCHO and [NHP]H. When we attempted to locate a similar metathesis pathway leading H[Si]OCHO to [Si](OCHO)$_2$, we were able to obtain a TS (i.e. TS6) similar to TS4 but the counterpart of TS5 could not be located. TS6 leads to an intermediate IM5 tending to dissociate, giving [NHP]$^+$ and an anionic component which can isomerize to IM7 easily (the details for the isomerization are given in Fig. S3†). Subsequently, [NHP]$^+$ extracts the H(–Si) atom in IM7 via TS7, giving [Si](OCHO)$_2$ and regenerating the catalyst [NHP]H. The metathesis process from IM3 to H[Si]
OCHO is energetically feasible with a RDS (rate determining step) barrier of 21.2 kcal mol\(^{-1}\) (TS5) relative to IM3. Yet, we speculated that the stage may proceed via an ionic mechanism because free HCO\(_2\) is available via the equilibrium (Scheme 2). The red pathway in Fig. 2A illustrates the ionic mechanism. Once IM3 dissociates, the resulting HCO\(_2\) attacks the Si\(^{1+}\) center of [Si]H\(_2\), forming a HCO\(_2\)−[Si]H\(_2\) complex (IM6\(^+\)). Although the nucleophilic attack is unfavorable by 10.2 kcal mol\(^{-1}\) mainly due to the entropic penalty of the association, HCO\(_2\) activates its trans Si–H bond significantly, as reflected by the stretched Si–H bond (\(R = 1.564\) Å in IM6\(^+\) versus 1.485 Å in [Si]H\(_2\)). Subsequently, the cationic species [NHP]\(^+\) extracts the activated H\(^+\) of the HCO\(_2\)−[Si]H\(_2\) complex (IM6\(^+\)) via a \(S_N2\)-like transition state TS8, resulting in H[Si](OCHO) and regenerating [NHP]H. Comparing the two mechanisms, the ionic mechanism is 3.0 kcal mol\(^{-1}\) (the energy difference of TS5 and TS8) kinetically more favorable than the metathesis mechanism. The lower TS8 compared to TS5 can be attributed to the more favorable trans Si–H bond activation by HCO\(_2\) in TS8, compared to the cis activation in TS5 (see Fig. 2B). The Si–H bond marked at 1.564 Å in IM6\(^+\) is activated more significantly than that marked at 1.498 Å in IM4. Thus, the dissociation of IM3 to free HCO\(_2\) and [NHP]\(^+\) essentially benefits the achievement of optimal trans activation of the Si–H bond in spite of the energy cost of 4.6 kcal mol\(^{-1}\) for the dissociation. For the conversion of H[Si]OCHO to [Si]OCHO\(_2\), because HCO\(_2\)− as a free species can attack H[Si]OCHO directly, forming IM7\(^+\), a TS similar to TS6 is not necessary. Overall, the transformation (2CO\(_2\) + [Si]H\(_2\) \(\rightarrow\) [Si]OCHO\(_2\)) is exergonic by 20.5 kcal mol\(^{-1}\) and the RDS barrier is 18.2 kcal mol\(^{-1}\) (metathesis mechanism) or 21.2 kcal mol\(^{-1}\) (metathesis mechanism), thus [Si]OCHO\(_2\) can be produced easily, in agreement with the experimental observation.

C–N bond formation (stage III). After forming [Si]OCHO\(_2\), a C–N bond starts to form (eqn (4)) in Scheme 3. Intuitively, the bond can be formed via the nucleophilic attacks of amine, illustrated by mode A and B in Scheme 3, yet the high barriers, 41.1 (mode A) and 31.6 kcal mol\(^{-1}\) (mode B), rule out the two modes, considering that the reaction could occur under mild conditions (see eqn (1)). We explored other alternatives discussed below.

C–N bond formation catalyzed by HCO\(_2\)−. As discussed above, HCO\(_2\)− is available via microscopic equilibrium (Scheme 2). Thus, we considered whether a HCO\(_2\)− ion can facilitate the C–N bond formation via H-bonding to the N–H bond of 1a (i.e. mode C in Scheme 3), because the bonding of the anionic species can enhance the nucleophilicity of amine 1a. Fig. 3 depicts the mechanism for eqn (4a) under the catalytic effect of HCO\(_2\)−, along with key optimized structures. First, HCO\(_2\)− and 1a form a H-bond complex IM8\(^+\), then the complex attacks [Si](OCHO)\(_2\) via TS9\(^+\), giving IM9\(^+\) with a C–N bond formed. Interestingly, the C–N bond formation shifts the N–H\(^{−}\)–O\(^{−}\)–H bond pattern (R(N−H\(^{−}\))/R(H\(^{−}\)–O\(^{−}\)) = 1.033/1.791 Å in IM8\(^+\) to the N−H\(^{−}\)–O\(^{−}\) pattern (R(N−H\(^{−}\))/R(H\(^{−}\)–O\(^{−}\)) = 1.617/1.031 Å in IM9\(^−\)). Meanwhile, the formal negative charge of HCO\(_2\)− is shifted to the O\(^{−}\)C\(^{−}\)O\(^{−}\) moiety, as reflected by the bond equalization of the two C–O bonds from 1.348/1.198 Å in [Si]OCHO\(_2\), to 1.379/1.396 Å in IM9\(^−\). The charge transfer shortens the O−O distance to 1.741 Å due to the attraction of Si\(^{1+}\) and (O\(^{−}\)\(^{2−}\)) and elongates the Si−O bond (from 1.683 to 1.816 Å) because of the disruption of the original Si–O single bond, resulting in the four-membered ring (SiO\(^{−}\)C\(^{−}\)O\(^{−}\)) in IM9\(^−\). Subsequently, the HCO\(_2\)− moiety in IM9\(^−\) swings to the O\(^{−}\) site by crossing a lower barrier (TS10\(^+\), 2.7 kcal mol\(^{-1}\) relative to IM9\(^−\)), giving IM10\(^+\), in which the four-membered SiO\(^{−}\)C\(^{−}\)O\(^{−}\) ring and the O\(^{−}\)–H\(^{−}\)–O\(^{−}\) H-bond pattern (R(O\(^{−}\)–H\(^{−}\))/R(H\(^{−}\)–O\(^{−}\)) = 1.569/1.011 Å) are maintained. TS11 leads IM10\(^+\) to the formamide product (1b) and IM11\(^−\). In addition to breaking the C–O\(^{−}\) and Si–O\(^{−}\) bonds to give 1b, TS11\(^−\) alters the O\(^{−}\)H\(^{−}\)–O\(^{−}\) H-bond pattern in IM10\(^−\) to the O\(^{−}\)–H\(^{−}\)–O\(^{−}\) H-bond pattern (R(O\(^{−}\)–H\(^{−}\))/R(H\(^{−}\)–O\(^{−}\)) = 1.045/1.455 Å) in IM11\(^−\). The dissociation of HCO\(_2\)− from IM11\(^−\) to regenerate the active HCO\(_2\)− species costs only 5.0 kcal mol\(^{-1}\). The mechanism discussed above indicates that HCO\(_2\)− is not just a H-bond partner to enhance the nucleophilicity of amine 1a. By altering the H-bond pattern between X−–H–O and X−H···O (X = N or O) and shifting the charge between the HCO\(_2\)− and O\(^{−}\)C\(^{−}\)O\(^{−}\) unit, HCO\(_2\)− catalyzes bond formations (i.e. C–N and Si–O\(^{−}\) bonds in IM9\(^−\)) and cleavages (i.e. C−O\(^{−}\) and Si–O\(^{−}\) bonds in IM10\(^−\)). It is interesting that CO\(_2\) can be activated to an active species to facilitate its transformation. Following the same mechanism in Fig. 3, eqn (4b) takes place, producing another formamide (1b) and silanol [Si](OH)\(_2\). Without going into detail (see Fig. S5† for the energy profile of eqn (4b)), we mention that the RDS barrier of eqn (4b) is 27.3 kcal mol\(^{-1}\), 5.5 kcal mol\(^{-1}\) higher than that of eqn (4a).

C–N bond formation facilitated by hydrogen transfer shuttle. The C–N bond formation through mode A and B involves a four-membered TS featuring hydrogen transfer (see Scheme 3). Thus a protic molecule such as water may act as a hydrogen transfer shuttle (H-shuttle)\(^{20,21}\) to facilitate the stage. In the present system, the possible H-shuttles could be water (trace water could not be excluded absolutely), N-methylaniline 1a, and silanol (HO[Si]OCHO and [Si](OH)\(_2\)), which are available when
the reaction is initiated. Using water as a representative, we characterize the H-shuttle-aided pathway (eqn (4)) through mode A, as illustrated in Fig. 4. Without going into detail, we mention that the water-aided C–N bond formation involves two hydrogen transfer steps, sequentially forming C–N and breaking C–O (CO₂ deoxygenation) bonds, as described by TS₁₂ and TS₁₃ for eqn (4a), respectively.

Table 1 compares the RDS barriers for eqns (4a) and (4b), mediated by various H-shuttles and HCO₂⁻. Note that, because the hydrogen transfers do not involve IM₃ or [NHP]⁺/HCO₂⁻ ions, their RDS barriers were measured relative to [Si](OCHO)₂ for eqn (4a) or HO[Si](OCHO) for eqn (4b). As compared, water is a more effective H-shuttle than amine 1a, which is consistent with our previous study of C–N bond formation in the dehydrogenative coupling of alcohol and amine.⁴⁰ Both HO[Si] OCHO and [Si](OH)₂ are better than water with HO[Si]OCHO being even better, which is due to the more polar O–H bond in silanol compared to that in water (see Fig. S6†). HCO₂⁻ is more effective than water but less effective than silanol.

For the formation of the C–N bond through mode B (Scheme 3), the water H-shuttle does not help much with only a slightly lower barrier (30.5 kcal mol⁻¹), compared to 31.6 kcal mol⁻¹ without the H-shuttle. The most effective H-shuttle, HO[Si] OCHO, in the case of mode A has a barrier of 27.3 kcal mol⁻¹ in the case of mode B, which is much higher than 18.8 kcal mol⁻¹ through mode A. We thus do not expect that other H-shuttles could aid the stage through the mode B mechanism more efficiently than that through mode A and did not pursue the mode further.

After characterizing the efficiency of these hydrogen transfer mediators in prompting C–N bond formation, we now discuss how the C–N bond could actually be formed. Both eqn (4a) and
(4b) are thermodynamically favorable, being exergonic by 9.9 and 6.9 kcal mol\(^{-1}\), respectively. We focus on the kinetics of the reactions using eqn (4a) as an example for simplicity.

It was reported that in the absence of \([\text{NHP}]\cdot\text{H}\) and \(\text{CO}_2\), \([\text{Si}](\text{OCHO})_2\) alone could react with \(1\a\) to give \(1\b\). As the efficiency of the reaction was not reported, our energetic results show that the reaction is able to take place, because the barrier for eqn (4a), when using water as a H-shuttle, is 26.4 kcal mol\(^{-1}\), which is somewhat high but in a reasonable range for a reaction to occur. Importantly, when the reaction is initiated to produce silanol, the silanol byproducts can promote the reaction more effectively, with lower barriers (see Table 1). In the presence of \([\text{NHP}]\cdot\text{H}\) and \(\text{CO}_2\), \(\text{HCO}_2^-\) plays the role of initiating the reaction rather than water, because the RDS barrier of 21.8 kcal mol\(^{-1}\) using \(\text{HCO}_2^-\) as a catalyst is much lower than 26.4 kcal mol\(^{-1}\) using a water H-shuttle as a promoter. As the reaction proceeds, more and more silanols (\(\text{HO}[\text{Si}]\text{OCHO}\) or \([\text{Si}](\text{OH})_2\)) are produced, thus, silanols take the role of \(\text{HCO}_2^-\) to promote C-N bond formation.

### Table 1 Comparisons of the RDS barriers for eqn (4a) and (4b), facilitated by various promoters

<table>
<thead>
<tr>
<th>Mediator</th>
<th>Eqn (4a)</th>
<th>Eqn (4b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{HCO}_2^-)</td>
<td>21.8(23.7)</td>
<td>27.3(29.2)</td>
</tr>
<tr>
<td>No (mode A)</td>
<td>41.1(43.0)</td>
<td>ND</td>
</tr>
<tr>
<td>Water (mode A)</td>
<td>26.4(30.2)</td>
<td>28.3(32.1)</td>
</tr>
<tr>
<td>Amine (1\a) (mode A)(^a)</td>
<td>28.7(32.5)</td>
<td>34.1(37.9)</td>
</tr>
<tr>
<td>(\text{HO}[\text{Si}]\text{OCHO}) (mode A)(^b)</td>
<td>18.8(22.6)</td>
<td>19.9(23.7)</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BOH%7D">\text{Si}</a>_2) (mode A)(^c)</td>
<td>20.4(24.2)</td>
<td>24.8(28.6)</td>
</tr>
<tr>
<td>No (mode B)</td>
<td>31.6(33.5)</td>
<td>ND</td>
</tr>
<tr>
<td>Water (mode B)</td>
<td>30.5(34.3)</td>
<td>ND</td>
</tr>
<tr>
<td>(\text{HO}[\text{Si}]\text{OCHO}) (mode B)</td>
<td>27.3(31.1)</td>
<td>ND</td>
</tr>
</tbody>
</table>

\(^a\) Complete pathway is given in Fig. S8. \(^b\) Complete pathway is given in Fig. S9. \(^c\) Complete pathway is given in Fig. S10. ND: not determined.

### 3.2 Mechanism for 2a methylation (eqn (2))

Kinjo et al.\(^{18}\) have applied an \([\text{NHP}]\cdot\text{H}\) catalyst to perform formylations of a range of primary and secondary amines. Intriguingly, 2,2,4,4-tetramethylpiperidine (\(2\a\)) and diisopropyldiamine (\(3a\)) were found to afford \(N\)-methylated amines, \(2c\) (eqn (2)) and \(3c\) (eqn (3)), respectively. In general, formamide (the formylation product) was considered to be the intermediate for the methylation of amine with \(\text{CO}_2\). The mechanism was also adopted to elucidate the methylation products (\(2c\) and \(3c\)). Nevertheless, we reasoned that this could not be true in the present catalytic system (\textit{supra infa}). Using eqn (2) as an example, we investigate the methylation mechanism.

The C-N bond in formylation is formed via the nucleophilic attack of amine (\(1\a\)) to \([\text{Si}](\text{OCHO})_2\) (see TS9\(^{\dagger}\) in Fig. 3). Alternatively, we speculated that the hydrides, either \([\text{Si}]\text{H}_2\) or \([\text{NHP}]\cdot\text{H}\), may compete with the amine to attack \([\text{Si}](\text{OCHO})_2\). Fig. 5 illustrates our computed pathway for 2a methylation, along with key optimized structures. Starting from \([\text{Si}](\text{OCHO})_2\), \([\text{NHP}]\cdot\text{H}\) first transfers its \(\text{H}^+\) to a formyloxy carbon of \([\text{Si}](\text{OCHO})_2\) with a barrier of 25.1 kcal mol\(^{-1}\) (TS16\(^{\dagger}\)). Under the catalytic effect of \(\text{HCO}_2^-\), \([\text{Si}]\text{H}_2\) offers its \(\text{H}^+\) with the higher barrier (27.1 kcal mol\(^{-1}\) at TS16\(^{\dagger}\)). Regardless of which hydride attacks \([\text{Si}](\text{OCHO})_2\), the hydride transfer results in an anionic four-membered intermediate IM14\(^{\dagger}\), which corresponds to IM9\(^{\dagger}\) in Fig. 3. Subsequently, the \([\text{NHP}]\cdot\text{H}\) cation attacks an O atom of the four-membered ring via TS17, breaking the C\(^{\dagger}\)-O\(^3\) and Si-O\(^2\) bonds, resulting in formaldehyde (\(\text{CH}_2\text{O}\)) and \([\text{NHP}]\cdot\text{H}[\text{Si}](\text{OCHO})_2\) (IM15). The \textit{in situ} generated \(\text{CH}_2\text{O}\) then attacks \(2\a\) electrophilically, forming a C-N bond and meanwhile transferring the (N-)H atom of amine to the carbonyl group of the formaldehyde moiety via TS18, resulting in IM16. The barrier for the process is 26.8 kcal mol\(^{-1}\) (TS18 relative to IM15), which is somewhat high but can be greatly lowered when a H-shuttle is used. For example, a water H-shuttle can lower the barrier to 14.1 kcal mol\(^{-1}\) (TS18\(^{\dagger}\)).

![Fig. 4 Free energy profile for the conversion of \([\text{Si}](\text{OCHO})_2\) + 2 × 1a → 2 × 1b + \([\text{Si}](\text{OH})_2\). Optimized structures of key stationary points are displayed in Fig. S7.† Energies are relative to \([\text{NHP}]\cdot\text{H}, \text{CO}_2, 1\a, \text{H}_2\text{O}, \text{and} \([\text{Si}](\text{OH})_2\) and are mass balanced.](image-url)
Subsequently, another [NHP]$^+$ attacks the hydroxyl group of IM16 via TS19$, leading to a carbocation species [IM17]$^+$ and [NHP]OH with a barrier of 23.3 kcal mol$^{-1}$ (TS19$^+$ relative to IM16 + IM3). After receiving a H$^{3-}$ of [NHP]H or [Si]H$_2$, the carbocation species converts to an N-methylated amine (2c). Our calculations showed that for this step, [NHP]H is a preferred hydride donor with a barrier of 16.6 kcal mol$^{-1}$ (TS20$^+$ relative to IM17$^+$ + IM3). An attempt using HCO$_2$ as to promote the H$^{3-}$ transfer of [Si]H$_2$ was not successful, and the geometric optimization to locate the H$^{3-}$ transfer TS indicated that the steric effect between the bulky amine and [Si]H$_2$ prevents the hydride transfer.

According to the methylation pathway (Fig. 5A), the reaction seems to consume the catalyst by forming [NHP]O[Si]OCHO (i.e. IM15) and [NHP]OH by-products. However, as detailed in ESI 2, the two intermediates can be recovered to catalyst [NHP]H feasibly in terms of both kinetics and thermodynamics.

The methylation mechanism involves formaldehyde and a carbocation species IM17$^+$ as the key intermediates. For the viability of formaldehyde, we call attention to the fact that Bontemps, Sabo-Etienne and coworkers experimentally detected formaldehyde in their Ru-catalyzed conversion of CO$_2$ to C$_2$ species with pinacolborane as a reducing reagent.$^{14}$ Previously, we predicted that formaldehyde could be involved in the NHC-
and Ni-catalyzed CO2 conversion to CH3OH. The involvement of a carboxylation species in CO2 conversion has not ever been reported. For the viability of the carboxylation species (IM17+), the cationic species must not form stable species (namely, IM17OCHO) with the anionic HCO2−, because a deep trap would raise the hydrogen transfer barrier from IM17+ + IM3 to TS20+ (Fig. 5A). To estimate the stability of IM17OCHO, we computed the reaction energy of eqn (5). The small endothermicity (1.8 kcal mol−1) of the equation indicates that IM17OCHO is only slightly more stable than IM3.

It is interesting to compare the roles of the [NHP]+ and HCO2− ions in formylation and methylation. In 1a formylation (Fig. 3), only the HCO2− component plays the catalytic role and [NHP]+ is a spectator. Differently, in 2a methylation (Fig. 5) the cationic component [NHP]+ plays the catalytic role, and [NHP]+ promotes the generation of CH3O (from IM14+ to IM15) and the carboxylation species (IM17+) from IM16.

3.3 The origins for chemoselectivities of formylation and methylation

The detailed characterizations of the mechanisms of eqn (1) and (2) facilitate our understanding of the chemoselectivities of the catalytic system. Using the conversion of the first formyloxy group of [Si](OCHO)2 as a representative case, we discuss the origins of the chemoselectivities. Key results for the conversion of the second formyloxy group of [Si](OCHO)2 (i.e. that in HO[Si]OCHO given in Table S1†) support the discussions below. According to the discussion in Section 3.2, the formylation/methylation preference stems from the competition between nucleophilic attacks of amine and hydride (i.e. TS9− in Fig. 3 and TS16 in Fig. 5) to [Si](OCHO). Table 2 compares the barriers of the two attacks for different amines. Note that the barrier for methylation is independent of amines. For 1a formylation, the barrier is 21.8 kcal mol−1, which is well below the barrier of 25.1 kcal mol−1 for methylation, thus eqn (1) prefers formylation. In contrast, the barrier (29.3 kcal mol−1, TS9-2a in Fig. 6) for 2a formylation is much higher than the barrier of 25.1 kcal mol−1 for its methylation, rationalizing the production of N-methylated amine (i.e. 2c) in eqn (2). The higher formylation barrier of 2a compared to 1a can be attributed to the greater steric effect in TS9−-2a than that in TS9−, as indicated by the shorter H1−H2 distance (2.112 Å) than that (2.261 Å) in TS9−. In addition, TS9−-2a suffers steric repulsion between H1 and H3.

The competition mechanisms rationalize the chemoselectivities of eqn (1) and (2), but the energetic results disagree with the reported experimental result of eqn (3), affording N-methylated amine 3c. The formylation barrier of 20.5 kcal mol−1 (TS9−-3a in Fig. 6A) for 3a is lower than that (25.1 kcal mol−1) for its methylation. On the other hand, comparing the structures of TS9−-3a and TS9− (the TSs for 3a and 1a formylations respectively), the H1−H2 distance (2.329 Å) in the former is even longer than that (2.261 Å) in the latter, indicating a smaller steric effect in TS9−-3a than in TS9−. In addition, the N atom in 3a bears more negative charge (−0.728e) than that (−0.658e) in 1a, indicating that 3a is more nucleophilic than 1a. Thus both the steric and electronic effect agree with the slightly lower formylation barrier (20.5 kcal mol−1) of 3a than that of 1a (21.8 kcal mol−1). We doubt that eqn (3) might actually produce formamide (3b).

To verify our computed mechanisms and the production of 3b in eqn (3), we performed experiments to study the reactions of 1a−3a (see ESI 3 for experimental details†). Scheme 4 shows our experimental results. Under the same experimental conditions, we were successful in reproducing the reported results of eqn (1), giving 1a in 96% yield (see eqn (6)). However, our study shows that 3a prefers to undergo formylation, affording formamide (3b) in 56% yield (eqn (8)), rather than N-methylated amine 3c as reported previously (eqn (3)), supporting our computational prediction. For 2a, under the same experimental conditions, we could only obtain traces of 2c. Based on our computed mechanism, we reasoned that the poor performance of the reaction could be due to (a) the barrier for methylation (25.1 kcal mol−1) being higher than that for formylation (e.g. 21.8 kcal mol−1 for 1a formylation) and (b) [NHP]+ being required to finally reduce IM17+ to 2c (see Fig. 5), but it could be consumed during the process reaching IM17+. Thus, we modified the experimental conditions as shown in eqn (7) of Scheme 4. Delightedly, under the modified conditions, the methylated amine 2c could be produced in 65% yield. Overall the experimental results corroborate our computational prediction satisfactorily.

We have shown that, in the present catalytic system, it is unlikely that methylation passes through formamide as an intermediate. We analyze why this is true. To further reduce formamide, the hydride (either [NHP]+ or [Si]H2) should transfer its H+ to the carbonyl carbon of formamide, thus the electrophilicity of the carbon should be a factor to determine
how favorably the formamide accepts a hydridic hydrogen of a hydride donor. Fig. 6B compares the NBO charges of formamides (1b–3b) with those of [Si](OCHO)₂ and HO[Si]OCHO. It can be found that the formyloxy carbon in [Si](OCHO)₂ and HO[Si]OCHO bears significantly more positive charge (>0.70e) than that in formamides (<0.58e). Thus [Si](OCHO)₂ and HO[Si]OCHO show stronger acceptor abilities for hydride than formamides.

Table 2  Comparisons of the barriers for formylation, methylation, and hydride transfer from [NHP]H and HCO₂⁻–[Si]H₂ to formamides a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Formylation</th>
<th>Methylation</th>
<th>Hydride transfer to formamide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔG°</td>
<td>ΔG°</td>
<td>ΔG°</td>
</tr>
<tr>
<td>1a</td>
<td>21.8(23.7)b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>29.3(31.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>20.5(22.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>18.8(20.7)</td>
<td>25.1(25.1)</td>
<td>27.1(29.0)</td>
</tr>
<tr>
<td>5a</td>
<td>20.7(22.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>17.3(19.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>22.5(24.4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

° All optimized structures of the transition states are displayed in Fig. S12. b Values in parentheses are the free energy barriers without corrections.

Fig. 6  (A) Comparing the structures of the transition states (TS9°, TS9°-2a, and TS9°-3a) resulting in 1a, 2a, and 3a formylations. (B) Comparing the NBO charges (in e) of [Si](OCHO)₂ and HO[Si]OCHO with those of formamides (1b–3b).
OCHO can be reduced more easily than formamides. Consistently, the hydride transfer barriers from $\text{[NHP]}\text{H}$ to $1\text{b}$, $2\text{b}$, and $3\text{b}$ are substantially higher (37.3–44.1 kcal mol$^{-1}$) than that (25.1 kcal mol$^{-1}$) to [Si](OCHO)$_2$. This is also true when [Si]H$_2$ is used as the hydride donor with HCO$_2^-$ as the promoter (see Table 2).

To further corroborate our conclusions, we calculated the RDS barriers for formylation of the other four amines (4a–7a in Table 2) reported in ref. 16. The barriers for formylation of the four amines, ranging from 18.8–22.5 kcal mol$^{-1}$, are all lower than the barrier for methylation (25.1 kcal mol$^{-1}$), in excellent agreement with the experimental fact that these amines prefer formylation. Again, the barriers for hydride transfers to their corresponding formamides (4b–5b) are substantially high (>34.6 kcal mol$^{-1}$). The high reduction barriers of formamides call attention to the sequential mechanism for understanding the methylation of amine with CO$_2$.

4. Conclusions

In this study, we have performed a DFT study to investigate the catalytic mechanisms of the 1,3,2-diazaphospholene ($\text{[NHP]}\text{H}$)-mediated formylation/methylation of amines (methyleneamine (1a)/2,2,4,4-tetramethylpiperidine (2a)) with CO$_2$ and hydro-silane (Ph$_2$SiH$_2$ = [Si]H$_2$) as a reducing reagent. Formylation of 1a proceeds via three stages, including hydrophosphination of CO$_2$, giving [NHP]OCHO (stage I), reaction of [NHP]OCHO with [Si]H$_2$ to form [Si](OCHO)$_2$ (stage II), and aminolysis of [Si](OCHO)$_2$ to form a C–N bond, finally affording formamide (stage III). Methylation of 2a shares the first two stages of formylation but is different in stage III. After stages I and II, the resultant [Si](OCHO)$_2$ is preferentially subjected to the attack of an [NPH]H hydride, resulting in formaldehyde which then couples with 2a to form a C–N bond in IM16. Subsequently, IM16 converts to a carbocation species. The methyl group is finally formed via hydride transfer of [NPH]H to the carbocation species. Thus, different from the general consideration that methylation passes through formamide as reduced intermediates of CO$_2$, the formylation and methylation in the present catalytic system are two competitive reaction channels. The chemoselectivity originates from the competition between amines and [NHP]H to attack the formyloxy carbon of [Si](OCHO)$_2$. If the attack of an amine (e.g. 1a) wins the competition, the transformation affords formamide (1b) and otherwise (e.g. 2a) results in N-methylated amine (2c). The reduction of formamides is highly kinetically unfavorable, which calls attention to the sequential mechanism for understanding amine methylation with CO$_2$.

On the basis of the detailed pathways, we have the following key findings in terms of reaction modes. The activation of CO$_2$ by [NHP]H establishes a microscopic equilibrium: [NHP]H + CO$_2$ ⇌ [NHP]OCHO ⇌ [NHP]$^+$ + HCO$_2^-$. The ions play catalytic roles to facilitate formylation with HCO$_2^-$ or methylation with [NHP]$^+$. In 1a formylation, HCO$_2^-$ initially forms a N–H…O (of HCO$_2^-$) H-bond complex with 1a to attack [Si](OCHO)$_2$. By altering the H-bond pattern between X–H…O and X–H…O (X = N or O) and shifting the formal charge between HCO$_2^-$ and the OCO unit in [Si](OCHO)$_2$, HCO$_2^-$ promotes C–N bond formation and CO$_2$ deoxygenation, finally resulting in formamide. However, it should be noted that, after the formylation is initiated, the silanol byproduct (either HO[Si]OCHO or [Si](OH)$_2$) is more effective than HCO$_2^-$ to promote the formylation. Formaldehyde and a carbocation (IM17$^+$) were characterized to be two important species to tunnel methylation and the generations of the species require the catalytic action of [NHP]$^+$.

Conflicts of interest

There are no conflicts to declare.

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