Predictive energetic tuning of C-Nucleophiles for the electrochemical capture of carbon dioxide

Highlights

CO₂ binding energy was calculated for a set of N-heterocyclic carbenes (NHCs)

CO₂ binding energy of NHCs is widely synthetically tunable

pKₐ, reduction potential, and CO₂ binding energy correlate linearly for NHCs

3D correlation enables easy prediction of CO₂ binding strength for novel NHCs

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Predictive energetic tuning of C-Nucleophiles for the electrochemical capture of carbon dioxide

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SUMMARY
This work maps the thermodynamics of electrochemically generated C-nucleophiles for reactive capture of CO₂. We identify a linear relationship between the pKa, the reduction potential of a protonated nucleophile (E_red), and the nucleophile’s free energy of CO₂ binding (ΔG/bind). Through synergistic experiments and computations, this study establishes a three-parameter correlation described by the equation

ΔG/bind = -0.78pKa + 4.28E_red + 20.95

for a series of twelve imidazol(in)ium/N-heterocyclic carbene pairs with an R² of 0.92. The correlation allows us to predict the ΔG/bind of C-nucleophiles to CO₂ using reduction potentials or pKas of imidazol(in)ium cations. The carbenes in this study were found to exhibit a wide range CO₂ binding strengths, from strongly CO₂ binding to nonspontaneous. This observation suggests that the ΔG/bind of imidazol(in)ium-based carbenes is tunable to a desired strength by appropriate structural changes. This work sets the stage for systematic energetic tuning of electrochemically enabled reactive separations.

INTRODUCTION
Lowering atmospheric concentrations of CO₂ to levels that will mitigate the effects of climate change will require substantial implementation of carbon-neutral and carbon-negative technologies, including carbon capture (Institute, 2020; National Academies of Sciences, Engineering, and Medicine, 2019). The development of optimal carbon capture materials requires a careful balance of the energetics of CO₂ binding to the proposed capture material. However, CO₂ binding free energies (ΔG/bind) are not easily experimentally accessible.

Among proposed materials for CO₂ capture and conversion, imidazolium salts have gained considerable attention due to the attractive liquid properties of their alkylated variants, including their favorable solvation of CO₂ gas as well as their high conductivity, which renders them uniquely suited for electrochemical applications (Kelemen et al., 2011; Sowmiah et al., 2009; Zhao et al., 2016). In addition to these favorable properties, imidazolium salts readily yield N-heterocyclic carbenes (NHCs) through deprotonation (Scheme 1B). Interestingly, electrochemical access to the free NHCs has been previously demonstrated as shown in Scheme 1A. Upon reduction, an imidazolium cation releases half of an H₂ equivalent and becomes a free NHC (Gorodetsky et al., 2004). The free NHC then exhibits reactivity with CO₂, as shown in Scheme 1C. Historically, the reaction of Scheme 1C was originally developed as a protection method for reactive NHCs (Voutchkova et al., 2007), and it has found applications in the synthesis of organometallics (Hahn and Jahnke, 2008) and catalysis (Luca and Fenwick, 2015; Luca et al., 2015; Riduan et al., 2009; Yang and Wang, 2014).

Using this reactivity, we now demonstrate a three-way correlation between the experimentally accessible reduction potential (E_red) of the imidazolium (Scheme 1A), the pKa of the imidazolium (Scheme 1B), and the CO₂ binding energy of the corresponding NHC (Scheme 1C). While the correlation between the pKa of an imidazolium (Scheme 1B) and ΔG/bind of the corresponding free NHCs (Scheme 1C) has been studied using density functional theory (DFT) on a set of 90 imidazoliums (Wang et al., 2018), it has not been related to the E_red of the imidazolium (Scheme 1A), which is a property that is routinely measured by standard electrochemical experiments (Gorodetsky et al., 2004). While the number of the imidazolium salts in this study is smaller (Figure 1), we map a landscape of CO₂ binding free energies spanning 15 kcal, 20 pKₐ units, and 1.7 V of potential.

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We investigate the relationship between $E_{\text{red}}$, $pK_a$, and $\Delta G_{\text{bind}}$ associated with reactions A–C in Scheme 1. The parameters are related due to their mutual dependence upon the electron density at the apical imidazolium carbon. Basicity and nucleophilicity are intrinsically related, with basicity being a subset of nucleophilicity. All nucleophiles are Lewis bases, but the term nucleophilicity is utilized to describe the affinity of a molecule to not only protons but also other electron-deficient molecules such as carbon dioxide. In essence, our correlation of $pK_a$ with the free energy of CO$_2$ binding ranks the nucleophilicity of an NHC against two types of electrophiles: protons and carbon dioxide.

Increasing the electron density of an imidazolium core causes it to have a more negative $E_{\text{red}}$ (Scheme 1A); a rise in electron density at a site of deprotonation lowers the stability of the deprotonated species and thus increases the $pK_a$ of the conjugate acid (Scheme 1B); and finally, a rise in electron density on a nucleophile corresponds to an increase in its nucleophilicity and thus its ability to attack an electrophile such as CO$_2$ is enhanced (Scheme 1C). Although we describe these general relationships to assert that the $E_{\text{red}}$, $pK_a$, and $\Delta G_{\text{bind}}$ of the twelve imidazol(in)ium cations presented in Figure 1 are correlated, analogous relationships generally apply to other potential molecular CO$_2$ capture substrates and thus the approach we use herein may be applied to other, more complex systems for redox-enabled CO$_2$ capture, such as quinones and N-nucleophiles (Wilcox, 2020). Unlike traditional electroswing systems which operate through cycles of binding CO$_2$ with cathodically generated nucleophiles followed by release of CO$_2$ in an electrochemical oxidation step, the electrochemical step of NHC generation and binding of CO$_2$ can be coupled with a thermal release step rather than an oxidation. The thermal release of CO$_2$ from NHC adducts is known (Van Ausdall et al., 2009; Luca and Fenwick, 2015), thus setting the stage for hybrid electrothermal CO$_2$ capture-release methodologies.

**RESULTS**

Before performing DFT calculations to investigate the relationship between free energy of CO$_2$ binding, reduction potential, and $pK_a$ for the set of imidazolium cations, we first sought to experimentally validate...
several assumptions about the system. Because imidazolium cations \( \text{ImH}^+ \) are aromatic, the reduction of \( \text{ImH}^+ \) to add an electron to the imidazolium \( \pi \)-system results in de-aromatization of the imidazolium ring. Prior studies have shown that aromatic hydrides exhibit a linear correlation between the first reduction potential of the oxidized hydride and the nucleophilicity of the hydride (Alherz et al., 2018; Ilic et al., 2018). To verify this correlation for imidazolium salts, we measured \( E_{\text{red}} \) for a family of imidazolium salts (Figure S1 and Table S1) using normal pulse voltammetry (NPV). While the influence of ion pairing and association on properties of imidazolium salts has been well documented in the ionic liquid literature (Tsuzuki et al., 2013; Voroshylova et al., 2018; Wang et al., 2015), the nature of the counterion’s effects on our measurements is minimized through the use of \( \text{NBu}_4\text{PF}_6 \), an electrolyte with a chemically stable, non-coordinating \( \text{PF}_6^- \) anion. Furthermore, we validated the observation that one-electron reductions of imidazolium cations produce free NHCs and verified that this applies to the analogous imidazolinium cations with non-aromatic, saturated backbones. We confirmed that the voltammetry responses of imidazolinium cations are associated with one \( e^- \) reductions using the method of Donadt et al. (Donadt et al., 2018) based on diffusion ordered spectroscopy (DOSY NMR) and NPV to quantify the number of electrons associated with the

Figure 1. Imidazol(in)ium-based NHCs used in the correlation studies
Structures of each compound under study. See also Figure S1 and Table S1 for applicable experimental values associated with each NHC. Imidazolium counterparts (protonated NHCs) are abbreviated as “NHC\(^+\)” in this work.
assumed one-electron reduction step (Scheme 1A and Figure S2); this is consistent with the observed one e⁻ reduction of imidazolium cations to produce free NHCs.

With these experimental validations in hand, we next computed the values of \( E_{\text{red}} \), \( pK_a \), and \( D_{\text{Gbind}} \) for each of the imidazolium derivatives using DFT based on the MN15/6-311+G(d,p) level of theory paired with the SMD solvent model as implemented in the Gaussian 16 quantum chemistry code (Frisch et al., 2016; Krishnan et al., 1980; Marenich et al., 2009; McLean and Chandler, 1980; Yu et al., 2016). The DFT-computed \( pK_a \) and \( E_{\text{red}} \) values we obtained agree with experiment (Chu et al., 2007; Dunn et al., 2017), with mean absolute errors (MAE) below 0.15 pK a units and 0.05 V, respectively. For additional computational details, please refer to the STAR methods, Figure S3 and S4, Tables S2–S4.

The calculated free energies of binding to CO₂ range from +5 to 10 kcal/mol, indicating that the equilibrium constant for CO₂ binding varies by over 10 orders of magnitude at 298 K. Consequently, this energy window suggests that the thermodynamics of NHC binding to CO₂ can be tuned over a wide range, for instance, by functionalization of NHCs with appropriate substituents to yield carbenes that bind CO₂ weakly or even nonspontaneously (e.g. 2CN-IMes) to strongly (e.g. Butyl-methyl imidazolium BMIM).

Notably, our calculations predict that four carbenes known to be stable in the presence of oxygen (2Cl-IMes, 2Br-IMes, 2Cl-IPr, and 2Br-IPr) (Arduengo et al., 1997; Furfari et al., 2015) have slightly negative \( D_{\text{Gbind}} \) values (−1.60 kcal/mol, −0.43 kcal/mol, −0.76 kcal/mol, and −0.50 kcal/mol, respectively). This observation has implications for direct air capture (DAC) of carbon dioxide, where stability to oxygen is a critical prerequisite for candidate materials. Weak CO₂ binders have an advantage for DAC processes whose thermodynamic efficiency also depends on low-energy release of CO₂ from the sorbent material (Lackner, 2013; Petersen and Luca, 2021).

Computations were then used to investigate three sets of correlations based on reactions a–c of Scheme 1 for twelve imidazol(in)ium cations. Figure 2 includes imidazolium cations that are not easily synthetically accessible. In these cases, correlations were performed using the calculated DFT values for \( E_{\text{red}} \) and \( pK_a \).

For imidazol(in)ium cations with known \( pK_a \) or \( E_{\text{red}} \), estimated \( D_{\text{Gbind}} \) for the corresponding NHC are readily obtained using the equations produced by the linear regressions shown in Figure 2. For instance, the \( D_{\text{Gbind}} \) in kcal/mol of the commercially available NHC precursor IMesH is estimated from either Equations 1 or 2:

\[
\Delta G_{\text{bind}} = 9.51 E_{\text{red}} + 19.13 \quad \text{Equation 1}
\]
\[
\Delta G_{\text{bind}} = -1.32 pK_a + 20.70 \quad \text{Equation 2}
\]

In the case of Equation 1, an experimental \( E_{\text{red}} \) for the compound is obtained within minutes using a routine electrochemical experiment such as NPV. Using the \( E_{\text{red}} \) value we measured of −2.64 V vs. Fc/Fc⁺ for IMesH, we then obtained an estimated \( \Delta G_{\text{bind}} \) for CO₂ binding from Equation 1 of −5.94 kcal/mol. Similarly, with a known \( pK_a \) value of IMesH in DMSO of 19.4 (Wang et al., 2018), Equation 2
is used to estimate a $\Delta G_{\text{bind}}$ of $-4.87 \text{ kcal/mol}$. These values compare favorably with the DFT-calculated $\Delta G_{\text{bind}}$ of $-5.78 \text{ kcal/mol}$, yielding errors of 0.16 kcal/mol (3%) and 0.91 kcal/mol (15%), respectively, and bracketing the calculated value.

Alternatively, in the case of imidazol(in)ium cations for which both the experimental $pK_a$ and $E_{\text{red}}$ are known, Equation 3 (Figure 3),

$$\Delta G_{\text{bind}} = -0.78pK_a + 4.28E_{\text{red}} + 20.95$$

Equation 3

is used to produce an estimated value for $\Delta G_{\text{bind}}$ with higher confidence than the individual correlations presented in Figure 2. For IMesH, this results in an estimated $\Delta G_{\text{bind}}$ of $-5.44 \text{ kcal/mol}$. This again

| ImH   | Exp. $E_{\text{red}}$ (V vs. Fc/Fc$^+$) | Exp. $pK_a$ | Est. $\Delta G_{\text{bind}}$ (kcal/mol) | DFT $\Delta G_{\text{bind}}$ (kcal/mol) | Error (%) |
|-------|--------------------------------------|-------------|------------------------------------------|----------------------------------------|-----------|
| IMesH | $-2.64$                              | 19.4        | $-5.4$                                   | $-5.8$                                 | 6         |
| IPrH  | $-2.63$                              | 19.3        | $-5.3$                                   | $-6.0$                                 | 12        |
| IMeH  | $-2.83$                              | 22.0        | $-8.3$                                   | $-8.3$                                 | 0.2       |
| EtMeH | $-2.87$                              | 22.1        | $-8.5$                                   | $-8.2$                                 | 4         |
| BMIM  | $-2.84$                              | 22.0        | $-8.3$                                   | $-8.4$                                 | 1         |
compares favorably to the DFT-calculated value of $\Delta G_{\text{bind}}$, this time yielding an error of only 0.34 kcal/mol (6%) and improving substantially upon the value obtained from the $pK_a$-only estimation. The results of using Equation 3 for all six compounds for which experimental values of $E_{\text{red}}$ and $pK_a$ are reported in Table 1.

Finally, as reduction potential is the most experimentally accessible value, it is desirable for various applications to predict the $pK_a$ of an imidazol(in)ium cation from its measured $E_{\text{red}}$. To do this, the two-way correlation equation of Figure 2 right is used (Equation 4),

$$pK_a = -8.08E_{\text{red}} + 0.92$$

Table 2 below compares computed and experimental $pK_a$s.

### DISCUSSION

We now establish a three-way correlation between the reduction potential, $pK_a$, and free energy of CO$_2$ binding for a set of imidazol(in)ium cations and their corresponding NHCs and use it to demonstrate the facile calculation of CO$_2$ binding energies from experimentally accessible electrochemical measurements. Four halogenated NHCs known to be stable to oxygen, a necessary sorbent trait for carbon capture applications in which oxygen may be present, were predicted to bind CO$_2$ with negative values of $\Delta G_{\text{bind}}$. Thermodynamic calculations for carbon capture (Petersen and Luca, 2021) suggest that materials that target energetically efficient reversible binding of CO$_2$ may be weak binders because strong binding results in a substantial energy penalty for the release phase. Although in this study we demonstrate our predictions on imidazol(in)ium-based NHCs, similar correlations will apply to other families of electrochemically responsive CO$_2$ capture molecular materials, thus enabling the mapping of energetics of a new chemical space for this application. Coupled with the known thermally triggered release of CO$_2$ from NHC-CO$_2$ adducts, our findings set the stage for energetic tuning of reactive separations in novel hybrid redox-thermal swing chemistries.

### Limitations of the study

Strong ionic association may have an impact on observed reduction potentials, resulting in values that differ substantially from those predicted by the correlations presented herein. While the subset of organic salts investigated is limited, we expect the correlation to hold across a large library of chemically similar species. However, steric effects may cause significant deviations from the established trends, as has been observed in the case of 1,3-di-3-butylimidazolium chloride (l'BuHCl).

### STAR★ METHODS

Detailed methods are provided in the online version of this paper and include the following:

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Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.103997.

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AUTHOR CONTRIBUTIONS
The manuscript was written through contributions of all authors. ORL, AA, and HP wrote the manuscript. AA and CM contributed the computational section, HP, TS, and CH contributed the experimental section. All authors have given approval to the final version of the manuscript. These authors contributed equally.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | | |
| 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (IMesHCl) | Strem Chemicals | Cat#07-0299; CAS-No. 141556-45-8 |
| 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride (SIMesHCl) | Strem Chemicals | Cat#07-4011; CAS-No. 173035-10-4 |
| 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (IPrHCl) | Strem Chemicals | Cat#07-0590; CAS-No. 250285-32-6 |
| 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride (SIPrHCl) | TCI Chemicals | Cat# B3157; CAS-No. 258278-25-0 |
| 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride (SIPrHBF4) | Sigma Aldrich | Cat# 693553-1G; CAS-No. 282109-83-5 |
| 1,3-dimethylimidazolium chloride (IMeHCl) | TCI Chemicals | Cat#D3341; CAS-No. 79917-88-7 |
| 1-ethyl-3-methylimidazolium hexafluorophosphate (EtMeHCl) | Alfa Aesar | Cat# L19762; CAS-No. 155371-19-0 |
| 1,3-di-t-butylimidazolium chloride (tBuHCl) | Strem Chemicals | Cat#07-0368; CAS-No. 157197-54-1 |
| 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide (BMIM TFSI) | Sigma Aldrich | Cat#77896-1G-F; CAS-No. 174899-83-3 |
| Tetrabutylammonium hexafluorophosphate | Sigma Aldrich | Cat#86874-100G; CAS-No. 3109-63-5 |
| Acetonitrile | Pharmco | Cat#300000DIS; CAS-No. 75-05-8 |
| Methanol | Macron Fine Chemicals | Cat#3016-16; CAS-No. 67-56-1 |

Software and algorithms

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| MN15 Functional | Yu et al., 2016 | N/A |
| 6-311+G(d,p) Basis Set | Krishnan et al., 1980 | N/A |
| SMD Solvent Model | Marenich et al., 2009 | N/A |
| McLean-Chandler (12s,9p) → (621111,52111) basis sets | McLean and Chandler, 1980 | N/A |
| uB97X-D Functional | Chai and Head-Gordon, 2008 | N/A |
| CPCM Solvent Model | Barone and Cossi, 1998 | N/A |
| Gaussian 16 | Frisch et al., 2016 | N/A |
| Optimized molecular coordinates | Data S1 | Used in Figure 2 |
| OriginPro 2019b | OriginLab | N/A |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Oana Luca (oana.luca@colorado.edu).

Materials availability
This study did not generate new unique reagents.

Data and code availability
All data reported in this paper will be shared by the lead contact upon request. This paper does not report original code. Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request. Optimized molecular coordinates used in the Figure 2 analysis are available for download as Data S1.
METHOD DETAILS

Electrochemical experiments

General methods

Reagents for use in electrochemical experiments were purchased from commercial sources and used as received except where otherwise noted. 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMesHCl), 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride (SIMesHCl), 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (IPrHCl), 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride (SIPrHCl), 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium tetrafluoroborate (SIPrH BF₄), 1,3-dimethylimidazolium chloride (IMeHCl), 1-ethyl-3-methylimidazolium hexafluorophosphate (IEtMeHCl), 1,3-di-t-butylimidazolium chloride (ItBuHCl), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI) were purchased commercially. Acetonitrile (MeCN) used in electrochemical experiments was freshly distilled and sparged with argon before use. Tetrabutylammonium hexafluorophosphate (NBu₄ PF₆) was recrystallized from methanol and dried overnight under high vacuum before use as supporting electrolyte.

Normal Pulse Voltammetry (NPV) experiments were performed using a silver wire single junction pseudo-reference electrode, a 3 mm diameter glassy carbon working electrode (MF-2012, BASI), and a platinum wire counter electrode. Standard NPV experimental conditions were 50 ms pulse width, 200 ms step time, and -10 mV pulse height. A vial filled with MeCN was used as a pre-bubbler to prevent solvent evaporation over the course of the experiment. Each imidazolium salt was dissolved in a 0.1 M NBu₄ PF₆ solution in MeCN and was degassed with argon prior to analysis. All glassware and needles used in the experiment and in solution transfer were oven-dried prior to use, and solvents and supporting electrolyte were dried as described above. The ferrocene/ferrocenium couple was used as an external standard reference for the applied potential.

Experimental reduction potentials

Each imidazolium salt was dissolved as a 1 mM solution in acetonitrile with 0.1 M NBu₄ PF₆ and subjected to the standard NPV conditions described above. The chloride salt was used for each imidazolium of interest, with the exception of BMIM TFSI. Experimental imidazolium reduction potentials were obtained by finding the potential at which the inflection point occurs in the NPV of the compound in question. This method was chosen over standard use of cyclic voltammetry E₁/₂ values due to the irreversible nature of the reduction and the improved ability of NPV to provide precise current responses with minimal interference from charging currents. This value was then averaged across three trials (with the exception of SIPr, 6 trials).

Electron quantification

NPV was used to determine the number of electrons associated with the reduction of SIPr using the method of Donadt et al. The number of electrons associated with a given electrochemical feature can be calculated using the Cottrell Equation, \( i = \frac{nFAC_o}{\sqrt{Dt}} \), in which \( i \) is limiting current (the current at the plateau of a feature), \( n \) is the number of electrons associated with the feature, \( F \) is Faraday’s constant, \( A \) is the electrode surface area, \( C_o \) is the bulk concentration of the analyte, \( D \) is the diffusion coefficient of the analyte, and \( t \) is the pulse width. The diffusion coefficient of SIPrH was first obtained by conducting Diffusion-Ordered Spectroscopy (DOSY) NMR on a sample of SIPrH BF₄ in deuterated MeCN. The diffusion coefficient was found to be 1.11*10⁻⁵ cm²/s. NPV (Figure S2) was then collected using a sample of 3.53 mg of the imidazolium salt IPrH BF₄ dissolved in a known amount of MeCN. The total sample mass was obtained before and just after the experiment to account for solvent loss during degassing and was used to calculate a final bulk concentration of 1.68 mM. Using the geometric electrode surface area of the 3 mm glassy carbon working electrode and the respective time parameter for each scan, the value of \( n \) can then be obtained with the Cottrell Equation.

Computational data

General methods

Quantum chemical density functional theory calculations have been conducted to compute the optimized geometries and energies of the carbene precursor, its protonated and reduced intermediates, and their adducts with CO₂. Frequency calculations were performed to ensure that the optimized geometries have no imaginary frequencies and obtain thermal and entropic corrections to the electronic energy to calculate Gibbs free energies. The DFT calculations utilize the Minnesota 15 (MN15) functional, Pople basis sets with polarization and diffuse functions 6-311+G(d,p), and acetonitrile solvent as described by the SMD...
solvent model (Krishnan et al., 1980; Marenich et al., 2009; McLean and Chandler, 1980; Yu et al., 2016) implemented within the Gaussian 16 software (Frisch et al., 2016). The energies obtained are used to calculate 3 main observable properties: pKₐ values, reduction potentials (of the protonated carbene intermediate), and the free energies of binding CO₂ to the resultant carbenes.

Similar computations were performed using the wB97xD/6-311+G(d,p)/CPCM method for comparison (Barone and Cossi, 1998; Chai and Head-Gordon, 2008; Cossi et al., 2003). The default cavity settings were additionally modified, as recommended by Mirzaei et al. (Mirzaei et al., 2019), such that the atomic radii for cavity estimates are modelled according to the Bondi radii rather than the fitted SMD-Coulomb parameters, and the calculations were carried out again. The three overall computational methods compared herein are therefore MN15/6-311+G(d,p)/SMD, MN15/6-311+G(d,p)/SMD-Bondi, and wB97xD/6-311+G(d,p)/CPCM.

All three DFT methods investigated are rather accurate in predicting pKₐ values compared to experimental values obtained from Ref. 18, as shown in Table S2. While the pKₐ and E_red values of 1′BuH were accurately predicted, this imidazolidine was omitted from the correlation plots because it deviates significantly from the trends obeyed by the other species where its computed ΔGbind value deviates by more than 6 and 7 kcal/mol from the expected values provided by the E_red and pKₐ correlations, respectively. This significantly different behavior most likely stems from the bulky 1′Bu groups of 1′BuH that hinder CO₂ binding more than planar Ph-based or smaller alkyl groups, resulting in a much less favorable ΔGbind value at comparable E_red and pKₐ values that are not shifted so dramatically because electron and proton transfers are not hindered as much as CO₂ binding.

While the SMD-Bondi cavity treatment has not been benchmarked rigorously in literature, we find that it succeeds in providing accurate pKₐ and E_red values (Tables S2 and S3), probably due to the nature of our fitting techniques discussed below. However, it seems to significantly over-stabilize the binding energies of CO₂ to carbenes. The SMD-Bondi cavity treatment significantly exaggerates the likelihood of binding (Table S4). Since this cavity method is the least tested across different systems and thus least trustworthy, we concluded that the default SMD treatment with the MN15 functional provides more realistic binding free energy values and opted to use this method for our correlations. It is also in agreement with the well-established wB97xD/CPCM method, within expected DFT errors (MAE = 3.2 kcal/mol).

**Acidity (pKₐ)**

pKₐ values are obtained by creating a linear fit between experimentally determined pKₐ values and the computed free energy difference G(XH⁺) − G(X). While it is common to estimate pKₐ values using an isodesmic approach or use a pre-determined free energy of solvated protons G(H⁺) (Alherz et al., 2018; Thapa and Schlegel, 2016), we argue that a linear fitting approach avoids any systematic errors in pKₐ predictions. Figure S3 shows the linear correlation described. The linear correlation is used to predict pKₐ values for other carbenes by computing the energies of the XH⁺ and X intermediates. This computation is performed for the energies obtained from each of the three DFT levels of theory for each imidazolidine (Table S4). This can also be used to extrapolate the expected free energy of an acetonitrile-solvated proton, G(H⁺) = −263.4 kcal/mol in close agreement with the experimentally determined value of −265.9 kcal/mol (Camaioni and Schwerdtfeger, 2005; Isse and Gennaro, 2010; Kelly et al., 2006; Marenich et al., 2014).

**Reduction potentials (E_red)**

Reduction potentials are first calculated according to the equation E⁰ = Gₓ⁻ – Gₓ⁻, where E⁰ₓ⁻ is the absolute redox potential of the ferrocene/ferrocinium reference couple (4.988 V in acetonitrile) (Namazian et al., 2010; Tossell, 2011). To avoid systematic underestimation of E_red (−0.3 V vs. experimental values), we then utilize a linear fitting approach between experimentally determined E_red values and the free energy differences G(X⁻) − G(X⁺). This computation is performed for the energies obtained from each of the three DFT levels of theory for each imidazolidine (Table S4).

**CO₂ binding free energy**

The free energy of CO₂ binding is computed according to the equation ΔGbind = G(XCO₂) − G(X⁻) − G(CO₂), where G(XCO₂) is the free energy of the NHC-CO₂ adduct, G(X⁻) is the free energy of the free...
NHC, and $G(CO_2)$ is the free energy of free CO$_2$. This computation is performed for the energies obtained from each of the three DFT levels of theory for each imidazolium (Table S4).

**Coordinates**

Data S1: Optimized molecular coordinates. All optimized molecular coordinates (MN15/6-311+G(d,p)/SMD level of theory) for the carbenes and intermediates of interest used in Figure 2 are provided in xyz format as a supplemental data.

**Correlation**

Best-fit analyses of each of the correlated parameters ($E_{\text{red}}$ vs. $pK_a$, $E_{\text{red}}$ vs. $\Delta G_{\text{bind}}$, $pK_a$ vs. $\Delta G_{\text{bind}}$, and $E_{\text{red}}$ vs. $pK_a$ vs. $\Delta G_{\text{bind}}$) were carried out in OriginPro 2019b.