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Design of Carbene-Based Organocatalysts for Nitrogen Fixation: Theoretical Study

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Supporting Information

ABSTRACT: Nitrogen fixation is a great challenge in solving the food supply of mankind. However N_2 activation is extremely hard. Up until recently, the investigated catalysts for N_2 fixation were based on metallic reducing agents. They are generally not environment friendly. We designed organocatalysts (carbenes) for nitrogen fixation using density functional theory (DFT) and *ab initio* theory. The reactivity of the carbene catalysts is mainly related to the electrostatic properties of the side chains. We compared the binding affinity to N_2 with various carbenes ($:CF_2$, $:CCl_2$, $:CBr_2$, and $:CI_2$). We revealed that the electron donating ability of the central carbene carbon is the most important factor for trapping N_2. Among heterocyclic carbenes, the cyclic diphospinocarbenes (PHC) represented a good candidate moiety for an efficient catalyst. We further designed the carbene based catalyst which has two carbene moieties to chelate N_2 and investigated the whole catalytic mechanism. The highest energy barrier of the entire catalytic cycle is 28.5 kcal/mol, which is comparable to the previously reported metallic catalysts. This demonstrates the possibility of novel organic catalysts for nitrogen fixation.

INTRODUCTION

Nitrogen is one of the most important biological elements. This ubiquitous element in simple biomolecules such as amino acids and DNA bases is thought to originate from atmospheric nitrogen, N_2. Although the conversion of nitrogen and hydrogen to ammonia is thermodynamically favorable, it may be achieved only by vigorous activation of the extremely strong N≡N bond, the dissociation of which requires ∼225 kcal/mol. To achieve this conversion, the famous Harber−Bosch process requires enormous energy and extreme conditions in the presence of a catalyst (∼800 K and 300 atm).[1] However, nature has already developed the means to break this triple bond under mild conditions, with the FeMo proteins.[2−5] Although these proteins exist only in some bacteria, exploring and developing effective catalysts for N fixation on an industrial scale by mimicking biological systems is extremely important and challenging. The proteins usually contain metal ions such as molybdenum and iron at the active site that are critical to activating N_2. Taking lessons from nature, exploring the effective catalysts for application in industry has been one of the greatest challenges.[6] There have been many studies for the metal containing catalysts for nitrogen fixation under mild conditions (298 K and 1 atm), wherein the metallic elements play critical roles. Chatt and co-workers reported on reducing N_2 to ammonia using the complexes $[M(N_2)_2[PR_3]_4]$ (M = Mo or W; R = alkyl or aryl).[7] Schrock and Yandulov discovered a catalyst based on the molybdenum complex with a specially designed triamidoamine ligand, hiptN$_3$N (tris-(hexaisopropylterphenyl)-triamidoamine), which is the first organometallic catalyst for ammonia synthesis at room temperature and under atmospheric pressure.[8] In this catalytic system, called the Schrock cycle, the molybdenum atom first binds the N_2 gas, and the broken charge balance of N_2 is restored by reducing agents supplying the protons and electrons until the N_2 converts to *two* ammonia molecules. Studt and co-workers' calculations were in agreement with the available experimental results,[9] basically supporting the mechanism proposed by Schrock and Yandulov. This complicated reaction proceeds through several intermediate steps. Yandulov and Schrock succeeded in the structural characterization of several presumed intermediates. In the same year, Reiher and co-workers revealed a more detailed mechanism to study the Schrock mechanism.[10]

The theoretically derived pathway involves a strictly alternating sequence of protonation and reduction and offers a detailed picture of the room-temperature conversion of N_2 into ammonia on a specially designed transition-metal center.

The organocatalytic processes pioneered by List[11] for organic synthetic reactions have several important advantages over the catalysis using the more traditional organometallics, for example, contributing to green chemistry. The metal-free organocatalysts such as the amino acid proline are environmentally benign and may work under milder conditions than the metal based catalysts. The vast potential of this important class of catalysts is being explored around the world,[12] and the use of natural or newly designed chiral organocatalysts may now lead to the formation of products in very high yield and of almost complete enantiomeric purity.[13] The N-heterocyclic carbenes (NHCs)[14] have proved to be one of the best established organocatalysts since they were proposed by Arduengo et al.,[15] behaving as nucleophiles with their lone

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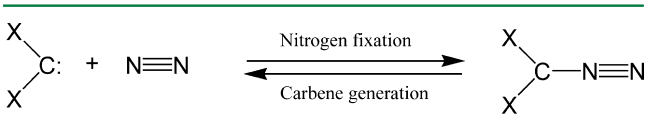
pair carbene electrons. The broad applications of N-heterocyclic carbenes (NHCs) in organic synthesis have been impressively demonstrated.

In this work, we focus on the possibility of using the organocatalytic systems for N fixation, using carbene's extremely strong reactivity. The general procedure producing a carbene is shown in Figure 1. One of the conventional



X=H, F, Cl, Br, I

Figure 1. Nitrogen fixation as a reverse process of carbine generation.

methods for producing carbenes from diazoalkanes, which serve as precursors to free the carbenes, is through a thermally or photochemically induced loss of N_2 (the reverse reaction is nitrogen fixation). Therefore, it is interesting to explore the possibility of obtaining stable carbene-N_2 molecules. We attempted to reduce the activation energy barrier of N_2 fixation by trying a variety of options for the attached group X. We investigate the effects of electronic properties of X on the control of the activity of carbene derivatives for simple systems. We studied which carbene moiety (including the cyclic carbenes) traps the N_2 molecule better by investigating the substituent effects. This information was further utilized to design and select more efficient carbene-based catalysts. We characterize the entire reaction pathway of nitrogen fixation with the chosen catalyst and find that the activation barrier is comparable to metal-based catalysts. Finally, we describe a very efficient N_2-chelating organo-catalyst using two carbene moieties. This understanding based on ab initio calculation could guide experiments, since a number of useful molecular structures, catalysts, drugs, nanomaterials, and nanodevices have nowadays been designed from such ab initio studies.[16]

COMPUTATIONAL DETAILS

We carried out quantum chemical studies employing the MP2 method with the aug-cc-pVDZ (aVDZ) basis set for calculating $X_2C{-}NN$ and heterocycliccarbene$-$NN. Stationary states are confirmed by ascertaining that all of the harmonic frequencies are real. The structure of the transition state is obtained by verifying that one and only one of the harmonic frequencies is imaginary, and also by carrying out the intrinsic reaction coordinate (IRC) analysis along the reaction pathway.

To study the catalytic cycles using PHC and bis(formyl-PHC)-pyridine catalysts, we optimized a series of cationic/neutral complexes by using the DFT method (M062X[17] with 6-31+G** basis set). Every protonation and reduction energy was explicitly calculated by combining each reaction with the corresponding conjugate reaction as shown in reaction 1 or 2 below, where [X] is an intermediate.

$$[X] + LutH^+ \rightarrow [XH]^+ + Lut \text{ (protonation)} \quad (1)$$

$$[XH]^+ + [Cp^*_2Cr] \rightarrow [XH] + [Cp^*_2Cr]^+ \text{ (reduction)} \quad (2)$$

The energy differences of $LutH^+ \rightarrow Lut$ and $[Cp^*_2Cr] \rightarrow [Cp^*_2Cr]^+$ are -227.3 and -103.2 kcal/mol, respectively. The reductant Cp_2^*Cr and its oxidized form were optimized by using the M062X/LANL2DZ method. The reported energies do not include zero point energy

RESULTS AND DISCUSSIONS

1. $X_2C{-}N_2$ Complexes. Figure 2a shows the calculated energy diagram and the shapes of orbitals of carbene. The

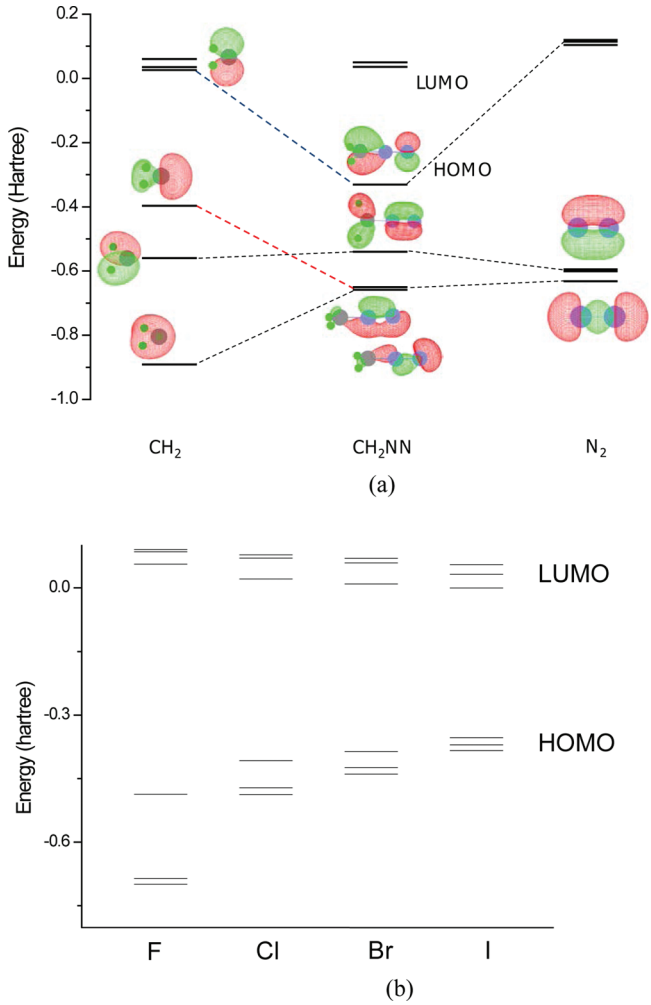


Figure 2. (a) Energies and shapes of :CH2, N_2, and N_2CNN orbitals. (b) Orbital energy diagram of halogenated carbenes. ($:CX_2$, X = F, Cl, Br, and I).

HOMO of the complex is mainly formed by the overlap of the carbene LUMO and the π^* orbital of N_2 (blue dashed line), resulting in backbonding of the metal$-$ligand complex. On the other hand, the $:CH_2$ HOMO donates electron density to nitrogen, forming a σ bond (red dashed line). As the energy of the carbene LUMO is lower, the HOMO (π^* bonding orbital) of the complex would be stabilized. Thus, it seems that the HOMO$-$LUMO gap of carbene is the predominant factor determining the stability of the carbene$-N_2$ complex.

We expected that the reactivity of carbenes would be controlled by the electrostatic variations of the side chains. We illustrated the effects of size variation of halogen atoms in Figure 2b and Table 1. As the size of the halogen atom increases, the HOMO$-$LUMO gap decreases, with more electron density on the central carbon atom (:C) and the elevated binding energies (ΔE_b) of the reverse reaction in Figure 1.

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Table 1. Binding Energies (ΔE) and Vibrational Frequencies (ν) of N−N Stretch for Halogenated Carbene−N_2 Complexes, and the NBO Charges of Carbon Atoms in Bare Halogenated Carbenes (MP2/aVDZ)

X	ΔE (kcal/mol)	ν(NN) cm^{-1}	charge (:C)
F			0.880
Cl	13.2	2344	0.045
Br	5.9	2331	−0.140
I	−3.1	2317	−0.362

Difluorocarbene ($:CF_2$) cannot trap N_2, but diiodocarbene ($:CI_2$) could form a stable complex (ΔE_b = 3.1 kcal/mol). Also, the natural bonding orbital (NBO) charges (Table 1) of the central carbon atoms of the carbenes are in agreement with those observed for the binding energies because the electron donating ability depends on the electron density of the central carbon. Thus, it may be inferred that the N_2 trapping capability depends on HOMO/LUMO energies and the electron density on the central carbon atom of the carbenes.

2. Heterocyclic Carbenes. Table 2 shows the binding energies (ΔE_b) and the vibrational frequencies of various heterocyclic carbenes and N_2, and the structures are described in the Supporting Information. The NHCs may not complex with N_2 as an end-on form (a). The side-on complex (b) is calculated to be in a stationary structure, but bonding seems to be unstable due to the large ΔE_b (+65.5 kcal/mol). Because the electron density is captured from the middle of the nitrogen molecule, the carbene makes two σ bonds. Oxazo-carbene (c) also failed to form a complex.

On the contrary, entries d−g, which are thiazo-, methyl-thiazo-, dithioene-, and dithioanecarbene, respectively, may form complexes with N_2. At the central carbon atoms of these carbenes, the electron densities are sufficient to donate to σ bonds of the complexes. Because the electron densities in d and e are trapped in the ring nitrogens, not in the central carbons in carbenes, the binding energies of these complexes are lower than those of f and g.

Cyclic diphospinocarbenes (PHCs, entries h and i) merit some attention.[18] The phosphorus atom is relatively soft and less electron-pulling than N, O, and S. Because of significantly large binding energy and *exothermicity*, we expected that PHC(i) could be a key component to build an efficient organocatalyst for nitrogen fixation.

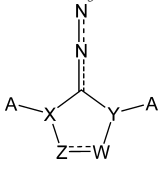
3. Catalytic Cycle of PHC. We calculated the N_2 converting process based on the trapping of N_2 by PHCs and the alternating sequence of protonation and reduction steps by the reducing agents (as Cp_2Cr and $LutH^+$) in which the positive and negative charges are generated stepwise. Figure 3 depicts the calculated catalytic cycle using the dimethyl-PHC carbene (i) catalyst.

With the starting complex **2** (PHC-N_2), the coordination of N_2 is calculated to be exothermic by 8.3 kcal/mol with an activation barrier of 22.0 kcal/mol. As shown in the energy profile (Figure 3b), the first proton−electron transfer to N_2 coordinated to carbene is considered to be a very important step because it generates the first activated "N_2" species. As in most cases of the nitrogenase, the first protonation is the hardest step. Either protonation by $LutH^+$ or reduction by $Cp_2{}^*Cr$ could be the first activation step of nitrogen activation. As demonstrated in the Supporting Information, the activation barrier of pathway 2 (protonation) is significantly lower than that of pathway 1 (reduction), indicating that the protonation-first pathway is more favorable than the reduction-first one.

The protonation process **2** to PHC−NNH^+ (**2**) is endothermic (+34.9 kcal/mol; Figure 3b). When the complex is protonated first, protonation to the central carbon is thermodynamically more favorable (by 21.6 kcal/mol) than protonation to the N_β atom. However, in the complex PHC−N_2···$LutH^+$, N_β protonation is more stable (by 5.1 kcal/mol) than protonation to the central carbon in the PHC−N_2 complex. In this pathway, H atoms add sequentially to a single N atom prior to N−N bond cleavage after the third hydrogenation. Subsequent reduction (**3** → **4**) is in an exothermic reaction (−52.6 kcal/mol) which gives a neutral intermediate. The next (**4** → **6**) steps (protonation/reduction) are a "diazenido" form for which the barrier is 5.3 kcal/mol. The **6** → **8** steps require an activation energy of 23.3 kcal/mol which is stabilized (−57.7 kcal/mol) by reduction (**8**) and N−N bond breakage (**8**). **8** is the complex of one ammonia molecule with the "nitridocarbene" moiety. During the H^+−NH_3 exchange step (**8** to **9**), one ammonia molecule is removed to be a nitrido form subsequent to reduction. After three protonation/reduction steps, **14** is formed. Another

Table 2. Binding Energies (ΔE) and Vibrational Frequencies (ν) of the N−N Stretch for Cyclic Carbene−N_2 Complexes (MP2/aVDZ)[a]

entry	X	Y	Z	W	A		ΔE	ν(NN) cm^{-1}
a	N	N	CH	CH	CH_3	imidazocarbene		
b	N	N	CH	CH	CH_3	imidazocarbene (side-on)	65.5	1735
c	N	O	CH	CH	H	oxazocarbene		
d	N	S	CH	CH	H	thiazocarbene	52.9	2143
e	N	S	CH	CH	CH_3	methylthiazocarbene	54	2244
f	S	S	CH	CH		dithioenecarbene	38.6	2216
g	S	S	CH_2	CH_2		dithioanecarbene	24.6	2256
h	P	P	N	CH	H	PHC	−2.8	2310
i	P	P	N	CH	CH_3	dimethyl-PHC	−8.8	2275



[a]Details are given in the Supporting Information (Figure S1).

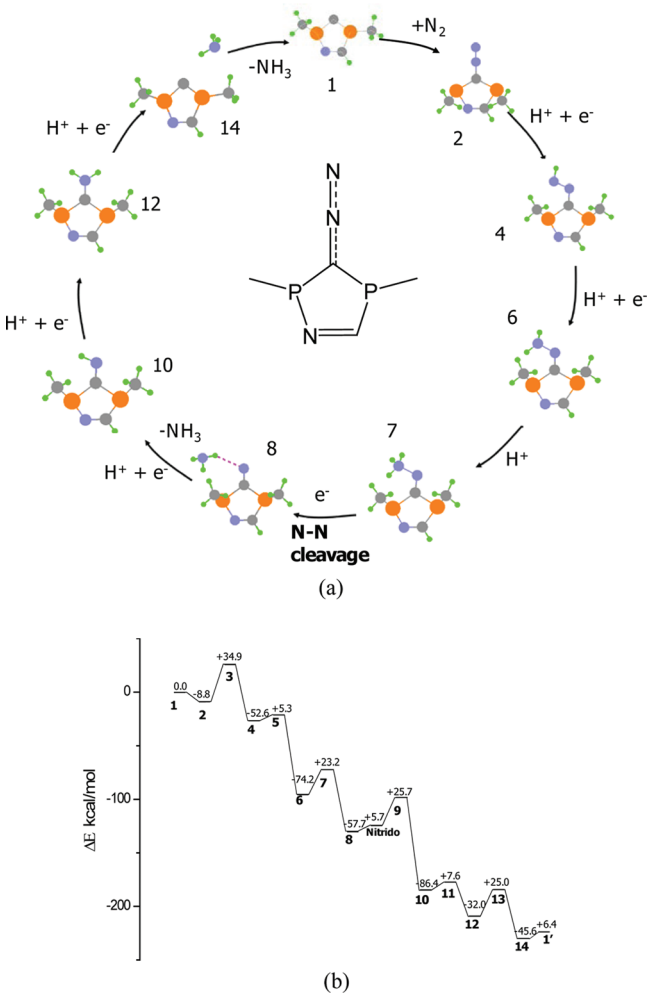


Figure 3. N_2 fixation process by PHC. (a) Structures in the alternating protonation/reduction process. (b) Energy profile.

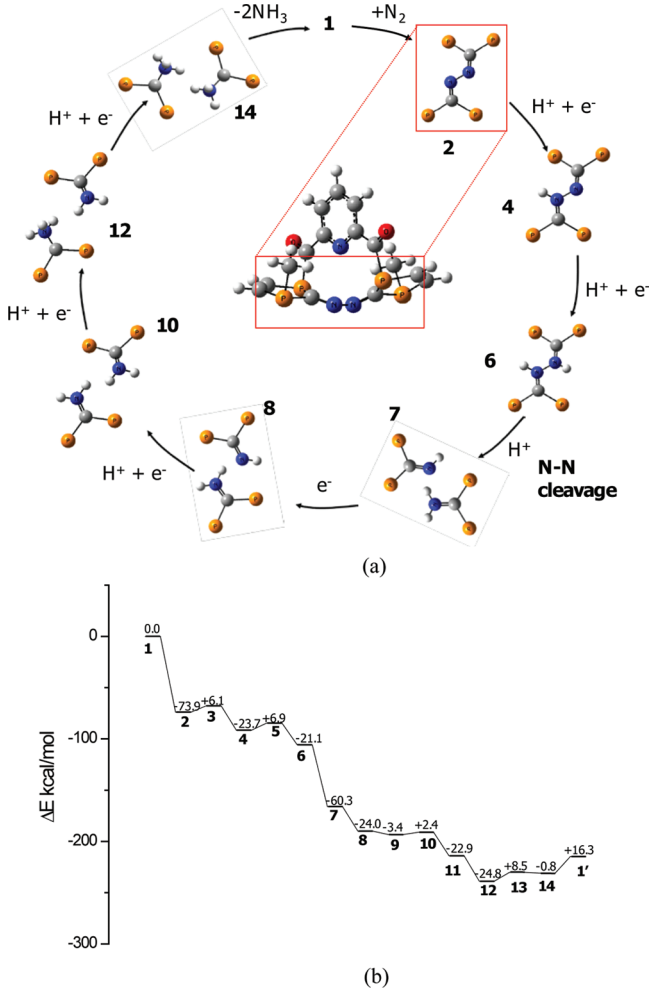


Figure 4. N_2 fixation process by bis-formyl-(PHC1) pyridine. (a) Structures in the alternating sequencing process (protonation/reduction). (b) Energy profile.

ammonia molecule is removed by ammonia/N_2 exchange, an endothermic step (+6.4 kcal/mol) completing one catalytic cycle. The energy of **1′** is accounted for in the energy conservation of the reaction: $N_2 + 6Cp_2^*Cr + 6LutH^+ \rightarrow 2NH_3 + 6Cp_2^*Cr + Lut$. Details are described in the Supporting Information (Figure S3).

4. Design the New Catalyst Including PHC Moieties. We describe a very efficient organocatalyst, bis(formyl-PHC)-pyridine, composed of a pyridine and two phosphoric carbenes. We used the formyl groups to link carbene parts (end-on bridging mode) and to prevent free rotation of the PHC moiety. The end-on bridging of N_2 is considered on the basis of three dinuclear titanium complexes,[19] containing N_2 in a linear μ-1,2 geometry. Here, we aim to achieve a strong activation of N_2 complexes using the end-on-bridging mode catalyst using the heterocyclic carbenes, which are designed onthe basis of bis(carbene)pyridine.[20]

The stable complex **2** (Figure 4) contains the C═N−N═C configuration. It is remarkable to observe that the extremely strong N≡N triple bond is changed to be a N−N single bond in this complex when N_2 is coordinated to the catalysts, which implies that a chelating system is much more favorable than a monocoordinating system to activate N_2. Figure 4 describes the structure of this catalytic system and the pathway. A N_2 molecule attaches to PHC first, which requires an activation energy of 28.5 kcal/mol (see the Supporting Information). Subsequently, the opposite side of N_2 and another PHC binds, as depicted in Figure 4a (red box). These steps are followed by the alternating sequence of protonation and reduction as described above. The first (**2** → **3**) and the second protonation steps (**4** → **5**) are endothermic by 6.1 and 6.9 kcal/mol, respectively. We also considered other possibilities of protonation. For example, the energy of protonation to O of the formyl group is too much higher (40 kcal/mol) than **2**. On the other hand, when the proton attaches to the central C atom of the carbene, the energy is ∼18.6 kcal/mol higher than **2**. However, these are less endothermic compared with the monobinding system. In next step of diazene (**6**) to hydrazido (**8**), the energy is exothermic by 84.3 kcal/mol and the N−N bond cleavage occurs. While there exist two small endothermic steps from **8** to **14**, the last protonation (**12**→**13**) only requires a small activation energy of 8.5 kcal/mol. After reduction (**14**), the two ammonia molecules are trapped by hydrogen bonding with the carbenes. In **14** → **1′**, the two ammonia molecules escape from the complex, and its energy is endothermic by 16.3 kcal/mol.

The N_2 chelating step (**1**→ **2**), for which the activation energy is 28.5 kcal/mol, has the highest energy barrier of the entire catalytic cycle. On the other hand, the most endothermic steps of the Chatt (with $LutH^+$ as a proton source) and Schrock

cycle are 49.8 and 21.1 kcal/mol, respectively. Therefore, this double-coordinating organocatalyst is expected to have catalytic activity comparable to that of the previously reported metallocatalysts.

CONCLUSION

We investigated the feasibility of the carbene-based organocatalysts for nitrogen fixation with quantum chemical calculations. We found out that the carbene catalysts could readily complex with N_2. The catalytic activity was controlled by varying the electrostatic property of side chains. We propose that chelating cyclic diphospinocarbenes could serve as efficient and benign organocatalysts for N_2 fixation that are comparable to metal-based catalysts. This shows the possibility of new organic catalysts for nitrogen fixation.

ASSOCIATED CONTENT

Supporting Information

The structures of heterocyclic carbene−N2 complexes, the N_2-fixation process of cyclic diphospinocarbenes, calculation of the total energy consumption of the total reaction N_2 + 6Cp2*Cr^+ + 6LutH^+ → 2NH_3 + 6Cp2*Cr^+ + 6Lut, and the N_2 chelating mechanism by bis(formyl-PHC)pyridine. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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