# Reversible O-Ylide Formation in Carbene/Ether Reactions

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Supporting Information

**ABSTRACT:** *p*-Nitrophenylchlorocarbene reacted reversibly with diethyl ether, di-n-propyl ether, or tetrahydrofuran (THF) to form O-ylides, which were visualized by their UV-visible spectroscopic signatures. Equilibrium constants  $(K_{eq})$  were determined spectroscopically and ranged from 0.10 M<sup>-1</sup> (di-*n*-propyl ether) to 7.5  $M^{-1}$  (THF) at 295 K. Studies of  $K_{eq}$  as a function of



temperature afforded  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and  $\Delta G^{\circ}$  for the di-*n*-propyl ether and THF/O-ylide equilibria.  $\Delta H^{\circ}$  was favorable for ylide formation, but  $\Delta S^{\circ}$  was quite negative, so that  $\Delta G^{\circ}s$  for the equilibria were small. Electronic structure calculations based on density functional theory provided structures, spectroscopic signatures, and energetics for the carbene/ether O-ylides.

# **I. INTRODUCTION**

We recently used laser flash photolysis (LFP) combined with UV-visible spectroscopy to demonstrate equilibration between  $\pi$ -complexes of carbenes and 1,3,5-trimethoxybenzene (TMB) and the individual reactants. Thus, phenylchlorocarbene and TMB equilibrate with a  $\pi$ -complex with  $K = 1250 \text{ M}^{-1}$  at 294 K and  $\Delta H^{\circ} = -7.1$  kcal/mol.<sup>1</sup> An analogous equilibrium operates between pentafluorophenylchlorocarbene, TMB, and the derived  $\pi$ -complex, with  $K = 3.2 \times 10^5 \text{ M}^{-1}$  at 294 K and  $\Delta H^{\circ} = -10.2$  kcal/mol.<sup>2</sup> A Hammett analysis of a family of equilibria between para-substituted phenylchlorocarbenes, TMB, and their  $\pi$ -complexes afforded  $\rho$  = 2.48, indicating that complexation is favored by electron-withdrawing, destabilizing substituents on the arylhalocarbene.<sup>3</sup>

Reversible  $\pi$ -complexation of arylhalocarbenes with very electron-rich substrates like TMB is thus reasonably general. However, with less electron-rich partners, such as anisole, O-ylide formation occurs competitively with  $\pi$ -complexation. For example, *p*-nitrophenylchlorocarbene (1, PNPCC) forms both O-ylidic and  $\pi$ -type complexes with anisole, although the latter are more stable and persistent.<sup>4</sup> On the other hand, PNPCC and simple ethers such as diethyl ether and 18-crown-6 form spectroscopically well-defined O-ylides.<sup>4</sup> PNPCC also forms carbonyl ylides with acetone and benzaldehyde<sup>5</sup> and an O-ylide with THF.6



Is O-ylide formation between PNPCC and simple ethers reversible? Does a demonstrable equilibrium exist between PNPCC, an alkyl ether, and its derived O-ylide? In an extensive study of halocarbene amides, Platz et al. presented indirect evidence<sup>7</sup> for equilibration between carbene 2, dioxane, and a derived O-ylide.<sup>8</sup> Here we provide *direct* spectroscopic evidence and computational support for reversible O-ylide formation between PNPCC and THF, diethyl ether, or di-*n*-propyl ether.

# 2. EXPERIMENTAL DETAILS AND COMPUTATIONAL **STUDIES**

**2.1. Experimental Details.** The preparation and purification of *p*-nitrophenylchlorodiazirine (3) has been fully described.<sup>4</sup> Solvents and ethers were commercial materials, used as received: pentane (>99%, anhydrous), heptane (99%, distilled), diethyl ether (anhydrous, certified ACS), di-n-propyl ether (99%, distilled), and THF (99%, distilled).



LFP experiments employed a XeF<sub>2</sub> excimer laser emitting 42-56 ns light pulses (full width at half-maximum) at 351 nm with 55–65 mJ power.<sup>9</sup> For these experiments, diazirine 3 was dissolved in pentane or heptane and the selected ether was added to the desired concentration. The final absorbance of 3 was 0.2-0.5 at 360 nm.

2.2. Computational Methods. Electronic structure calculations were carried out using density functional theory (DFT)<sup>10</sup> methodologies implemented in the Gaussian 09 suite of programs.<sup>11</sup> Ground state geometry optimizations of carbene and solvent monomers and dimeric carbene-solvent complexes

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**Figure 1.** Calibrated UV—vis spectrum of PNPCC in heptane (circles) and in 0.049 M THF in heptane (triangles),<sup>20,21</sup> 100 ns after the laser pulse. PNPCC absorptions at 308 and 628 nm; the PNPCC/THF *O*-ylide absorption is at 452 nm.

(O-ylides) were carried out using the dispersion-corrected B97D,<sup>12</sup> M06,<sup>13</sup> M06-2X,<sup>13</sup> or wB97XD<sup>14</sup> exchange-correlation functionals and  $6-311+G(d)^{15}$  basis sets (B97D/6-311+G(d), etc.). General solvent effects were incorporated via the polarizable conductor self-consistent reaction field model (CPCM)<sup>16</sup> with the default parameters for *n*-pentane or heptane provided in Gaussian 09. Geometry optimizations of both idealized gas and simulated solution phase structures were conducted with tight convergence criteria (opt=tight) and enhanced numerical integration grid sizes (integral(grid=ultrafine)). Vibrational frequencies (unscaled), evaluated at the optimized structures with enhanced integration grids, formed the basis for the calculation of zero-point energy (ZPE) contributions. Standard thermodynamic corrections (based on harmonic oscillator/rigid rotor approximations and ideal gas behavior) were then applied to the computed energies to derive (standard) enthalpies (H; T =298.15 K) and free energies (*G*; T = 298.15 K, P = 1 atm).<sup>17</sup> We equate the raw differences in free energies obtained from the CPCM calculations with reaction enthalpies and then apply ZPE and thermal entropic corrections. The reaction free energies presented in Table 3 correspond to a reference state of 1 M concentration for each species participating in the reaction and T = 298.15 K.

Excited state calculations (transition wavelengths ( $\lambda$ ) and oscillator strengths (f)) at optimized B97D/6-311+G(d) ground state geometries utilized the time-dependent DFT formalism<sup>18</sup> and the hybrid B3LYP functionals (TD-B3LYP/6-311+G(d))//B97D/6-311+G(d)).<sup>19</sup> Assignment of a particular electronic transition ( $\pi \rightarrow p, \sigma \rightarrow p$ , or  $\pi \rightarrow \pi^*$ ) was based on inspection of the largest transition amplitudes for the excitation and by visualization of the contributing MOs.

# 3. RESULTS AND DISCUSSION

**3.1. PNPCC and THF.** In the absence of added ethers, LFP of diazirine 3 in heptane generates PNPCC (1). Its calibrated<sup>20</sup> UV-vis spectrum (Figure 1) displays a dominant  $\pi \rightarrow p$  absorption at 308 nm and a weaker  $\sigma \rightarrow p$  absorption at 628 nm.<sup>21</sup> The computed  $\pi \rightarrow p$  absorbance of PNPCC is at 309 nm (f = oscillator strength = 0.5784), whereas the energy of the carbenic center localized  $\sigma \rightarrow p$  transition is significantly underestimated,  $\lambda_{calc} = 897$  nm (f = 0.0013).<sup>22</sup>

With 0.049 M added THF, there is a decrease in the carbene absorbance at 308 nm, coupled with the appearance of a signal assigned to PNPCC/THF *O*-ylide 4 at 452 nm; in pure THF, the ylide absorption is red-shifted to  $\sim$ 490 nm.<sup>23</sup> We calculate a



**Figure 2.** Time dependence of the decay of absorbance for (a) PNPCC in heptane at 316  $\text{nm}^{24}$  in the absence of THF (green), (b) PNPCC in heptane at 316  $\text{nm}^{24}$  in the presence of 0.049 M THF (blue), and (c) ylide 4 (red) at 452 nm. The black lines superimposed on the experimental traces correspond to the exponential fits.

Table 1. Kinetics of Decay of PNPCC and O-Ylides

PNPCC,		<i>,</i>	PNPCC	O-ylide <sup>a</sup>
no ether $k_{decay}$	ether	(conc., M)	$k_{decay}$	$k_{\text{decay}}^{b}$
0.48 (0.02)	$\mathrm{THF}^{c}$	(0.049)	0.84 (0.06)	1.0 (0.1)
	$Et_2O^d$	(2.33)	0.71 (0.06)	0.9 (0.1)
	n-Pr <sub>2</sub> O <sup>c</sup>	(2.05)	0.79 (0.04)	0.92 (0.07)

<sup>*a*</sup> Kinetics are in the presence of added ether. <sup>*b*</sup> All rate constants are in units of  $10^7 \text{ s}^{-1}$ . Errors are shown in parentheses. <sup>*c*</sup> Solvent is heptane.



**Figure 3.**  $A_{316}/A_{460}$  absorbance ratios for PNPCC and *O*-ylide 4 vs time (ns) after the laser pulse. The THF concentrations in heptane are 0.07 M ( $\triangle$ ), 0.14 M ( $\square$ ), 0.28 M ( $\diamondsuit$ ), and 1.06 M ( $\times$ ).<sup>26</sup>

strong absorption at 456 nm for 4 in simulated heptane; cf. Table 3, below.



Is there an equilibrium established between PNPCC, THF, and ylide 4? We note that the decay of the carbene and ylide signals conforms to similar kinetics; cf. Figure 2.<sup>24</sup> The rate constants derived from exponential fitting of the decays in Figure 2 are collected in Table 1. The rise of the absorptions in each trace (with apparent rate constants of  $\sim 1.5 \times 10^7 \text{ s}^{-1}$ ) are a

function of the laser pulse width; they do not represent rate constants for formation of the carbene or ylide.<sup>25</sup>

In the THF experiments, the rate constants for the decay of PNPCC and its THF *O*-ylide (4) are comparable. The kinetic linkages between  $k_{decay}$  for PNPCC and ylide 4 are consistent



**Figure 4.** Average values of  $A_{316}/A_{460}$  vs 1/[THF] (M<sup>-1</sup>) for PNPCC and *O*-ylide 4 in heptane at 295 K, 80–160 ns after LFP of diazirine 3. The slope of the correlation line is  $0.135 \pm 0.005$  M, r = 0.998. See Table S-1 in the Supporting Information for the numerical values of the experimental points.



**Figure 5.** Average values of  $A_{316}/A_{476}$  vs  $1/[\text{Et}_2\text{O}]$  (M<sup>-1</sup>) for PNPCC and *O*-ylide **5** in pentane at 295 K, 80 – 160 ns after LFP of diazirine **3**. The slope of the correlation line is 6.65 ± 0.11 M, *r* = 0.999. See Table S-1 in the Supporting Information for the numerical values of the experimental points.



**Figure 6.** Average values of  $A_{316}/A_{468}$  vs  $1/[Pr_2O] (M^{-1})$  for PNPCC and *O*-ylide **6** in heptane at 295 K, 80–160 ns after LFP of diazirine **3**. The slope of the correlation is  $9.16 \pm 0.38$ , r = 0.997. See Table S-1 in the Supporting Information for the numerical values of the experimental points.

with equilibration of these species. Analogous linkages are observed for the *O*-ylides formed from PNPCC and diethyl ether (**5**) or di-*n*propyl ether (**6**); cf. Table 1.

To determine  $K_{eq}$  for the PNPCC/THF system, we require the relative intensities of the carbene absorption at 316 nm<sup>24</sup> and of ylide 4. The latter absorbs at 490 nm in pure THF, but its maximum is found at 452–468 nm at the THF concentrations of 0.070–1.06 M used in our determination of  $K_{eq}$ . Therefore, we measured the ylide absorbance at 460 nm, the average wavelength of the absorption maxima in the considered THF concentration range.

As illustrated in Figure 3,  $A_{316}/A_{460}$ , the PNPCC/ylide 4 absorbance ratio is relatively constant at several THF concentrations between about 80 and 160 ns after LFP generation of the carbene. During this time interval, the carbene and its THF ylide are at their maximum concentrations and in relatively stable equilibrium.<sup>26</sup>

We plotted calibrated<sup>20</sup> average  $A_{316}/A_{460}$  absorbance ratios in the 80–160 ns time interval vs the inverse of the THF concentrations between 0.07 and 1.06 M, and we obtained the linear correlation shown in Figure 4. To determine the equilibrium constant,  $K_{eq}$ , we use computed oscillator strengths (f) in place of the experimentally unknown extinction coefficients ( $\varepsilon$ ) of PNPCC and 4. Thus, we calculate  $K_{eq}$  from the following relation:  $K_{eq} = (\varepsilon_{carbene}/\varepsilon_{ylide})(1/slope) = (f_{carbene}/f_{ylide})(1/slope),^{1,2}$ where  $f_{carbene}$  (0.5784) is the computed oscillator strength of PNPCC at 309 nm, and  $f_{ylide}$  (0.5688) is the computed oscillator strength of ylide 4 at 456 nm (see Table 3 below and the Supporting Information). The slope of the correlation line in Figure 4 is 0.135  $\pm$  0.005 M, r = 0.998, and we obtain  $K_{eq} =$ (0.5784/0.5688)(1/0.135 M) = 7.5  $\pm$  0.3 M<sup>-1</sup> at 295 K for the equilibrium [PNPCC + THF  $\rightleftharpoons$  4]. We estimate that the ratio  $f_{carbene}/f_{ylide}$  accurately reproduces the desired ( $\varepsilon_{carbene}/\varepsilon_{ylide}$ ) ratio to within a factor of 2.

**3.2.** PNPCC and Diethyl Ether or Di-*n*-propyl Ether. Similar analyses are carried out for the reactions of PNPCC with diethyl ether, affording *O*-ylide **5**, and of PNPCC with di-*n*-propyl ether, affording *O*-ylide **6**. For PNPCC and diethyl ether (Et<sub>2</sub>O), *O*-ylide **5** absorbs at 476 nm,<sup>4</sup> and a plot of calibrated average values of  $A_{316}/A_{476}$  vs  $1/[\text{Et}_2\text{O}]$  gives the correlation shown in Figure 5, where the slope =  $6.65 \pm 0.11$  M and r = 0.999. The computations (cf. Table 3) predict absorption of ylide **5** at 444 nm (f = 0.6138). Therefore,  $K_{eq} = (0.5784/0.6138)(1/6.65 \text{ M}) = 0.142 \pm 0.002 \text{ M}^{-1}$  at 295 K for the equilibrium [PNPCC + Et<sub>2</sub>O  $\Rightarrow$  **5**].

Diethyl ether is volatile, raising concern about the accuracy of its putative concentrations. Therefore, we conducted a parallel series of experiments with its less volatile analogue, di-*n*-propyl ether (Pr<sub>2</sub>O). *O*-Ylide **6**, from PNPCC and Pr<sub>2</sub>O, absorbs at 468 nm. A plot of calibrated average values of  $A_{316}/A_{468}$  vs  $1/[Pr_2O]$  affords the correlation shown in Figure 6, where the slope is 9.16  $\pm$  0.38 M and r = 0.997. The computations (cf. Table 3) predict absorption of ylide **6** at 446 nm (f = 0.6107).

Table 2. Equilibria of PNPCC and Alkyl Ethers							
ether	ylide	$\lambda_{\max}$ (nm)	$K_{\mathrm{eq}}^{a} \left( \mathrm{M}^{-1} \right)$	$K_{\mathrm{rel}}{}^{a,b}$	$\Delta H^{ m o}$ (kcal/mol)	$\Delta S^{ m o}$ (eu)	$\Delta G^{\mathrm{o}a}(\mathrm{kcal/mol})$
THF	4	460	$7.5\pm0.3$	1.0	$-11 \pm 1$	$-32\pm3$	$-1.19\pm0.02$
Et <sub>2</sub> O	5	476	$0.142\pm0.002$	0.019			
Pr <sub>2</sub> O	6	468	$0.103\pm0.004$	0.014	$-6.5\pm0.9$	$-27\pm3$	$1.33\pm0.02$
a	bp 1						

<sup>*a*</sup> At 295 K. <sup>*b*</sup> Relative to  $K_{eq}$  for [THF + PNPCC  $\Rightarrow$  4].

Therefore,  $K_{eq} = (0.5784/0.6107)(1/9.16 \text{ M}) = 0.103 \pm 0.004 \text{ M}^{-1}$ at 295 K for the equilibrium [PNPCC + Pr<sub>2</sub>O  $\rightleftharpoons$  6].

The measured equilibrium constants for PNPCC forming *O*-ylides with THF, Et<sub>2</sub>O, and Pr<sub>2</sub>O are collected in Table 2. The ordering of  $K_{eq}$ , by ether substrate, is THF > Et<sub>2</sub>O  $\approx$  Pr<sub>2</sub>O, with relative  $K_{eq}$ s of 1.0, 0.019, and 0.014, respectively. THF affords the most favorable carbene/*O*-ylide equilibrium, 50–70 times more favorable than Et<sub>2</sub>O and Pr<sub>2</sub>O. The [THF + PNPCC  $\rightleftharpoons$  4] equilibrium is thermodynamically favorable and lies modestly on the product side, whereas the equilibria with Et<sub>2</sub>O or Pr<sub>2</sub>O lie on the reactant side.

**3.3. Enthalpy and Entropy of O-Ylide Formation.** In order to extract the thermodynamic parameters governing these equilibria, we examined the temperature dependence of  $K_{eq}$  for the THF and  $Pr_2O$  substrates; we excluded Et<sub>2</sub>O because of its volatility. We monitored  $A_{316}/A_{460}$  vs 1/[THF] or  $A_{316}/A_{468}$  vs  $1/[Pr_2O]$  to determine  $K_{eq}$  at five or six different temperatures in the range  $285 \le T \le 323$  K. The data obtained in these determinations appear as Figures S-1 and S-2 in the Supporting Information, while the slopes, *Y*-intercepts, and  $K_{eq}$  values derived from these correlations at each temperature are collected in Table S-2.



**Figure 7.** Plot of  $\ln K_{eq}$  (M<sup>-1</sup>) vs 1/T (K<sup>-1</sup>) for the equilibrium [PNPCC + THF  $\Rightarrow$  4]. The slope (5312) affords  $\Delta H^{\circ} = -10.6 \pm 1.0$  kcal/mol, and the *Y*-intercept (-15.9) gives  $\Delta S^{\circ} = -31.6 \pm 3$  eu. The correlation coefficient is r = 0.986.



**Figure 8.** Plot of  $\ln K_{eq}$  (M<sup>-1</sup>) vs 1/T (K<sup>-1</sup>) for the equilibrium [PNPCC +  $Pr_2O \rightleftharpoons 6$ ]. The slope (3250) affords  $\Delta H^o = -6.46 \pm 0.9$  kcal/mol, and the *Y*-intercept (-13.4) gives  $\Delta S^o = -26.7 \pm 3$  eu. The correlation coefficient is r = 0.964.

Table 3. Computed Properties of O-Ylides<sup>a</sup>

3.4. Computational Studies. Electronic structure calculations based on density functional theory provide structures and energetics for PNPCC-ether O-ylides and rationalize their electronic absorption spectra. We have applied four exchangecorrelation functional combinations (B97D,12 M06 and M06- $2X_{1}^{13}$  and wB97XD<sup>14</sup>) and  $6-311+G(d)^{15}$  basis sets toward the computation of ground state properties (idealized gas phase conditions). The thermodynamic parameters ( $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ) for O-ylide formation produced by the chosen functionals are quite similar (Table S-3 in the Supporting Information); the enthalpies generated by the B97D set of functionals show, by a small margin, the overall best agreement with experimental observations. At the B97D/6-311+G(d) level, the computed O-ylide formation enthalpies are  $\Delta H^{\circ} = -10.6$  kcal/mol for 4 and -9.1 kcal/mol for 6, whereas the measured values are -11 and -6.5 kcal/mol, respectively (Table 2). When solute-solvent interactions (continuum dielectric model, model heptane solvent) are included in the geometry optimizations, the resulting enthalpies for formation become more favorable by ca. 2.7 kcal/mol ( $\Delta H^{\circ}$  = -13.3 kcal/mol for 4 and -11.7 kcal/mol for 6; Table 3). The increased thermodynamic stability of the O-ylides is accompanied by a reduction in the length of the polar carbene-ether C-O bond by ca. 0.03 Å (Table 3). All the tested functionals include dispersion corrections, but only B97D does not include exact (Hartree-Fock) exchange. Inclusion of exact exchange appears to increase the computed energies of O-ylide formation, and all the tested hybrid functionals (M06, M06-2X, and wB97XD) produce too large enthalpies (Table S-3). The effect is particularly evident in the enthalpies obtained with the M06-2X functionals, which incorporate approximately twice as much exact exchange as M06 or wB97XD.

However, the computed entropies for *O*-ylide formation are far more negative ( $\sim$ -43 eu, Table 3) than observed ( $\sim$ -30 eu, Table 2), independent of the functional combinations used (Table S-3) or the inclusion of continuum solvent (Table 3). Due to the overestimation of the formation entropies, the computed Gibbs free energies are strongly dominated by the large positive  $-T\Delta S^{\circ}$  term and are generally unfavorable (Table 3); consequently, the computed equilibrium constants are too small in magnitude. However, the [PNPCC + THF = 4] equilibrium is computed to be most favorable with an equilibrium constant approximately 10–60 times larger than the equilibrium

ether/ O-ylide	е С-О (Å)	$\Delta H^{ m o}$ (kcal/mol)	$\Delta S^{ m o} \; ({ m cal}/({ m mol}\;{ m K}))$	$\Delta G^{ m o}$ (kcal/mol)	$\lambda_{\max}^{b,c}$ (nm)	$f^{b,c}$	K (rel)
THF/4	1.476(1.450)	-10.6(-13.3)	-43.1(-43.1)	2.3(-0.5)	456	0.5688	1.0(1.0)
$Et_2O/5$	1.477(1.450)	-8.3(-11.1)	-43.5(-42.3)	4.7(1.5)	444	0.6138	0.016(0.036)
$Pr_2O/6$	1.481(1.451)	-9.1(-11.7)	-43.1(-42.3)	3.8(0.9)	446	0.6107	0.076(0.094)

<sup>*a*</sup> Calculations are B97D/6-311+G(d) (thermodynamics) and TD-B3LYP/6-311+G(d)//B97D/6-311+G(d) (UV-vis). Values in parentheses refer to calculations in which geometries were optimized including solvent (heptane) corrections; see computational details for the computation of reaction enthalpies and free energies. <sup>*b*</sup> In simulated heptane. <sup>*c*</sup> The  $\pi \rightarrow p$  absorption of PNPCC is computed at 309 nm, *f* = 0.5784.



Figure 9. (a) B97D/6-311+G(d) computed structure for PNPCC-Pr<sub>2</sub>O O-ylide 6. (b) HOMO of 6. (c) LUMO of 6.

constants for species **5** and **6**, in qualitative good agreement with experimental observations.

Figure 9a illustrates the conformer of lowest energy for PNPCC-Pr<sub>2</sub>O O-ylide 6 (analogous computed structures of 4 and 5 are available as Figure 4 in ref 4). The computed electronic transitions (Table 3) are blue-shifted by only 10-20 nm relative to the experimental peaks and thus compare favorably (Table 2). The identifying absorption near 450 nm arises as the result of a very pure (>95%) HOMO  $\rightarrow$  LUMO transition, which contains significant charge-transfer character. The HOMO is a relatively well-localized lone pair (essentially of  $\pi$ -type symmetry) on the carbene carbon with some admixture from the phenyl ring; the LUMO is a phenyl  $\pi^*$  orbital with considerable contributions from the *p*-NO<sub>2</sub> substituent (parts b and c of Figure 9, respectively). Neither the HOMO nor the LUMO contains much O(ether) character, which rationalizes the insensitivity of the PNPCCether O-ylide signature transition, in energy and intensity, to the specific nature of the alkyl ether.

# 4. CONCLUSIONS

*p*-Nitrophenylchlorocarbene reacts reversibly with diethyl ether, di-*n*-propyl ether, or tetrahydrofuran (THF) to form *O*-ylides. These can be visualized by their UV—vis spectroscopic signatures. Equilibrium constants ( $K_{eq}$ ) could be determined spectroscopically and ranged from  $0.10 \text{ M}^{-1}$  (di-*n*-propyl ether) to 7.5 M<sup>-1</sup> (THF) at 295 K. Studies of  $K_{eq}$  as a function of temperature afforded  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and  $\Delta G^{\circ}$  values for the di-*n*-propyl ether and THF/*O*-ylide equilibria.  $\Delta H^{\circ}$  was favorable for ylide formation, but  $\Delta S^{\circ}$  was quite negative ( $\sim$ -30 eu). Therefore  $\Delta G^{\circ}$ s for the equilibria were small,  $\sim$  -1.2 kcal/mol for THF and +1.3 kcal/mol for di-*n*-propyl ether. Electronic structure calculations based on density functional theory provided structures, spectroscopic signatures, and energetics for the carbene/ ether *O*-ylides. Comparisons of the computed and experimental data were generally satisfactory.

# ASSOCIATED CONTENT

**Supporting Information.** Figures S-1–S-2; Tables S-1–S-3; complete reference to Gaussian 09; B97D/6-311+G-(d) optimized geometries and absolute energies of THF; Et<sub>2</sub>O, Pr<sub>2</sub>O, **4**, **5**, and **6**; TD-B3LYP/6-311+G(d)//B97D/6-311+G-(d) electronic excitation energies and oscillator strenths for THF, Et<sub>2</sub>O, Pr<sub>2</sub>O, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Calibration corrects the raw UV–vis absorptions for wavelength-dependent variations in sample absorptivity (including precursor diazirine), xenon monitoring lamp emission, and detector sensitivity.

(21) In the uncalibrated spectrum in pentane, reproduced in ref 4, the  $\pi \rightarrow$  p absorption appears at 316 nm, and the  $\sigma \rightarrow$  p absorption at 628 nm is much more pronounced.

(22) Thus, the interaction between the phenyl  $\pi$ -type orbitals and the (formally empty) carbene p orbital leads to a computed  $\sigma$ -p (HOMO-LUMO) gap in PNPCC, which is too small. The tendency of DFT to underestimate the separation between occupied and unoccupied levels for weakly interacting systems, and thus of TD-DFT to underestimate the electronic excitation energies when local, time-independent functionals

are employed, has been documented; see, e.g., Dreuw, A.; Weisman, J. L.; Head-Gordon, M. J. Chem. Phys. 2003, 119, 2943–2946.

(23) The UV-vis absorption of THF ylide 4 is reported at  ${\sim}510$  nm in pure THF; see Figure 3 in ref 6a.

(24) The absorbance vs time traces in Figure 2 were determined at 316 nm, where our detector system is 40% more sensitive than at 308 nm.

(25) Carbene 1 is very likely formed from excited diazirine 3 on the picosecond time scale, faster than the time resolution of our nanosecond LFP system. See, for example, Zhang, Y.; Burdzinski, G.; Kubicki, J.; Vyas, S.; Hadad, C. M.; Sliwa, M.; Poizat, G.; Buntinx, G; Platz, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 13784–13790. *O*-ylide 4 also appears to form from carbene 1 and THF faster than our ~60 ns time resolution.

(26) At times >200 ns, scatter increases due to decay of the species and a diminished signal/noise ratio. At times <60 ns, the carbene and ylide absorptions are within the laser pulse width.