

**Scheme 1.** The three membered ring structure of oxaziridine molecule exhibiting inversion at the nitrogen center. ‘R’ represents an (in)organic group.

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**Fig. 1.** Adiabatic ionization energies (IE) and relative energies (ΔE) are calculated at the CCSD/cc-pVTZ//CCSD(T)/CBS level of theory. The cartesian coordinates of the structures are provided in Table S7. Bond lengths and angles are given in picometers and degrees, respectively.

**Fig. 2.** PI-ReTOF mass spectra measured at photoionization energies of (A) 10.49 eV and (B) 9.50 eV during the temperature program desorption (TPD) phase of the irradiated methane (CH4) - nitrogen monoxide (NO) ices.

**Fig. 3.** Temperature program desorption (TPD) profiles measured at (A) m/z = 45 (CH4 / NO), (B) m/z = 46 (13CH4 / NO), and (C) m/z = 48 (CD4 / NO) using a photon energy of 10.49 eV. TPD profiles of m/z = 45 (CH4 / NO) at photoionization energies of (D) 9.95 eV (E) 9.92 eV and (F) 9.50 eV. Errors in the photon energies are ± 0.0001 eV.

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**Fig. 4.** Computationally predicted reaction pathways of singlet (blue) and triplet (black) carbene (CH2) with nitrosyl hydride (HNO). The CCSD/cc-pVTZ//CCSD(T)/CBS energies are given in kJ mol-1 with respect to the separated reactants. The CPMCSCF/TZVPP//CCSD(T)/CBS mini­mum-energy crossing points (MSX) are shown for inter system crossing (ISC) pathways as waved arrows. Geometrical parameters of the species depicted are provided in Figures S12-S14 and coordinates are tabulated in Table S8. Bond lengths and angles are given in picometers and degrees, respectively.