Isolation and characterization of a triplet nitrene

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Abstract

Free nitrenes of R–N are short-lived intermediates in a variety of nitrogen-involved transformations. They feature either a singlet ground state or a triplet ground state, depending on the electronic properties of the substituents R. Triplet arylnitrenes typically undergo facile ring expansion to azacycloheptatetraenes, making their isolation in the condensed phase highly challenging. Herein, we present the synthesis, isolation and characterization of an isolable triplet arylnitrene supported by a bulky hydrindacene ligand. The high stability is largely attributed to the sufficient steric hindrance and effective electron delocalization imparted by the supporting ligand. Electron paramagnetic resonance spectroscopy in conjunction with highly correlated wavefunction based ab initio calculations unambiguously demonstrated its triplet ground state with axial zero-field splitting $D = 0.92\ \mathrm{cm}^{-1}$ and vanishing rhombicity $E/D = 0.002$. This work not only presents a long-sought reaction intermediate, but also provides in-depth insights into the reaction mechanisms involving nitrenes.

Introduction

Nitrene-involved reactions represent one of the most practical approaches for synthesizing nitrogen-containing molecules.[1, 2] Nitrenes were first proposed as short-lived intermediates in the Lossen rearrangement by Tiemann in 1891,[3] while the parent nitrene, HN, was detected merely in the interstellar space.[4] Free nitrenes of R–N possess six valence electrons at monovalent nitrogen atoms.[5] Generally, they prefer a triplet ground state, in which two unpaired electrons singly occupying two 2p orbitals have parallel spins, whereas the corresponding singlet state featuring antiparallel spin is less favored primarily because of the loss of exchange stabilization for electrons of like spin (Fig. 1). The electronic ground state and the geometric structure thereof are highly dependent on the electronic properties of the substituents. Presently, a series of fleeting nitrenes have been trapped and investigated by using ultrafast spectroscopy, matrix isolation spectroscopy, and electron paramagnetic resonance (EPR) spectroscopy, as well as theoretical calculations.[5-9]

Due to their extremely high reactivity and short lifetimes, the isolation of free nitrenes in the condensed phase still presents a highly challenging task. The pioneering work of a persistent trityl radical in 1900 by Gomberg[10] instigates the isolation of transient intermediates under standard laboratory conditions with rational chemical strategies.[11-14] In 1988, the group of Bertrand obtained the first stable singlet (phosphino)(silyl)carbene,[15] followed by the report of a crystalline *N*-heterocyclic carbene by Arduengo and coworkers three years later.[16] Nowadays, carbenes are widely leveraged as common chemical reagents in chemical research.[17-20] These striking findings demonstrated that once thought-of short-lived highly reactive species might be tamed and routinely applied as valuable reagents.

As an important class of reactive intermediates, substantial efforts have been devoted to accessing stable nitrenes.[2] Currently, they are mostly stabilized by coordination to transition metals,[21-24] while free nitrenes are still scarce. Bertrand and coworkers[25] also reported the first phosphinonitrene **I** stable at ambient temperature (Fig. 1). It has a singlet ground attributed to the effective π-stabilization of the vacant N 2p orbital caused by the lone pair of electrons at the phosphorus atom. In contrast, the isolation of triplet nitrenes is much more difficult due to their open-shell character, rendering them highly susceptible to side reactions. Schneider and coworkers[26-28] utilized a photocrystallographic method to structurally characterize triplet platinum- and palladium-substituted nitrenes **II**, which are quenched by crystal lattices at low temperatures. However, these triplet metallonitrenes cannot be isolated at ambient temperature. We recently demonstrated that hydrindacene ligands are an efficient platform for stabilizing one-coordinate main group compounds owing to the presence of a well-shielded pocket to accommodate reactive main group elements.[29-35] In this contribution, we present the synthesis, isolation and characterization of an isolable triplet nitrene supported by a hydrindacene substituent. EPR spectroscopic measurements in conjunction with highly correlated wavefunction based ab initio calculations unambiguously demonstrated its triplet ground state with axial zero-field splitting $D = 0.92$ cm^{-1} and vanishing rhombicity $E/D = 0.002$. Moreover, the reactivity of the isolated nitrene was preliminarily investigated.

Results and Discussion

Synthesis and characterization of 2

It is well recognized that aromatic nitrenes readily undergo facile ring expansion to seven-membered azacycloheptatetraenes.[36] We surmised that ring expansion might be impeded by a highly rigid backbone with substantial steric hindrance, leading to stable nitrenes. Therefore, we attempted to isolate nitrenes with hydrindacene ligands developed by our group.[37, 38] The azide precursor, M^{s}Fluid*-N_3 **1**, was prepared through the reaction of the lithium salt of the supporting ligand with tosyl azide. With **1** available, we first studied the stability of the photolytic product in different solvents (Supplementary Information Fig. S1-S6). It turns out that it is very unstable in 2-MeTHF and decays rapidly from a red solution with characteristic peaks located at 410 and 520–580 nm in the UV/Vis absorption spectrum to a pale yellow solution at 298 K. Fortunately, it is stable in benzene-D_6 and fluorobenzene solutions at 283 K, but decomposes slowly at 298 K.

Accordingly, the photolysis of **1** was carried out in benzene solution at 0 ^{o}C with an ultraviolet (UV) lamp (313 nm), and a deep red solution was formed after 5 hours. Measurements with ^{1}H NMR spectroscopy hinted at the formation of an NMR-silent product, implying its paramagnetic ground state. After the workup, nitrene M^{s}Fluid*-N **2** was isolated as a red solid in 52% yield (Fig. 2a). Red crystals of **2** suitable for single-crystal X-ray diffraction analysis were grown from benzene solution. It crystallizes in the monoclinic space group $I2/a$ (Fig. 2b). For comparison, amine M^{s}Fluid*-NH_2 **3**, synthesized through hydrogenation of **1** with $LiAlH_4$, crystallizes in the orthorhombic space group $P2_12_12_1$ (Supplementary material Fig. S8). The C–N distance (1.320(3) Å) in **2** is substantially shorter than that in amine **3** (1.404(5) Å), and is comparable to that (1.327(2) Å) of a nitrene recently reported by Beckmann et al.,[39] yet it marginally exceeds the C = N double bond length in a diaminobenzoquinoneimine (1.293 Å),[40] indicative of its significant double bond character. Consistently, **2** exhibits considerable bond length alteration in the central phenyl ring in comparison to that of **3** (0.038 vs. 0.011), i.e., the difference in the average lengths of longitudinal C–C bonds relative to those of transverse bonds to the C–N bond, suggesting a pronounced quinoid character due to delocalization of the unpaired electrons centered at the nitrogen atom.[41] These geometric features combined with the NMR findings strongly support **2** as a free nitrene, and resonance structure 2A exhibiting a C = N double bond, as depicted in Fig. 2a, contributed considerably to its ground-state electronic structure.

Characterization by EPR spectroscopy

The X-band EPR spectrum of powder sample of **2** recorded at 10 K exhibited a set of complicated features ranging from 195 to 1320 mT in addition to trace $S = 1/2$ paramagnetic impurities that account for < 1% of the total intensity. The signal of **2** can be satisfactorily simulated with an standard $S = 1$ spin Hamiltonian with $g_{\text{iso}} = 2.00$, $D = 0.92\ \text{cm}^{-1}$, and $E/D = 0.002$. As shown in Fig. 2c, the principal derivative signal appearing at ~ 670 mT is assigned to the transition within the upper two levels in the xy plane defined by the **D** tensor. More importantly, the looping transition[42] between the $M_s = 0$ and $M_s = -1$ levels manifests itself in the two turning points[43],[44] along the z direction; one negative peak is readily identified to be located at 1320 mT and the other positive one at 640 mT. Moreover, a much weaker yet discernible resonance is detected at ~ 195 mT, which is attributed to the forbidden transition between $M_s = \pm 1$ with the external magnetic field, B_0, along the z direction. In fact, it gains intensities from the admixing of $M_s = 0$ into $M_s = \pm 1$ induced by B_0 away from the z direction. All these transitions allowed us to precisely determine D and E/D provided that the **g** tensor was assumed to be isotropic with $g_{\text{iso}} = 2.00$, which has been invariably observed for related nitrenes.[5] The D value thus obtained falls into the usual range of 0.66 to 1.07 cm^{-1} measured for aromatic nitrenes generated by in situ photolysis of aromatic azides in solvent matrixes at low temperatures.[5]

Theoretical calculations

To elucidate the electronic structure of **2**, we undertook detailed wavefunction based multireference CASSCF[45]/NEVPT2[46] (CASSCF = the complete active space self-consistent field, NEVPT2 = N-electron valence perturbation theory up to the 2nd order) calculations. To reduce computational costs, a truncated model (**2'**) was employed, in which the alkyl substituents on the supporting ligand were replaced by hydrogen atoms. An active space was chosen to distribute 10 electrons into 10 orbitals, including N–C σ and σ*, N 2p orbitals, as well as the six π orbitals of the Ph ring. Theoretical results suggested that **2′** possesses a triplet ground state that is 19.5 and 34.3 kcal/mol lower in energy than the open- and closed-shell singlet states, respectively. As shown in Fig. 3, the dominant electron configuration of the triplet ground state is $(\text{Ph}\ \pi_{1,2,3})^6(\text{N–C}\ \sigma_z)^2(\text{N-Ph}\ \pi_4^*)^1(\text{N}\ 2p_x)^1(\text{Ph}\ \pi_{5,6,7}^*)^0(\text{N–C}\ \sigma_z^*)^0$, which accounts for 82% of the wavefunction. Because of the nearly vanishing energy separation between the N and C 2p atomic orbitals, there exists pronounced π-bonding that shifts electron density from N $2p_y$ into the Ph π* orbitals as indicated by the parentage of the N $2p_y$ atomic orbital in the singly occupied molecular orbital (SOMO) labelled as π_4^* being merely 43%. The N–Ph interaction thus features considerable double bond character, consistent with the computed Mayer bond order of 1.82 and the noticeable contribution of resonance structure 2A to the ground-state electronic structure. In line with this view is the sufficiently large spin density on the central phenyl group, in particular the para-position C4 atom that possesses 0.34 spin density. In addition, CASSCF(10, 10)/NEVPT2 calculations averaged on one triplet and two singlets predicted that **2** predicted $D = 0.88\ \text{cm}^{-1}$ and $E/D = 0.017$, both are in reasonable agreement with experimental results. The *D* value was computed to nearly exclusively arise from the first-order spin-spin coupling, whereas the second order spin-orbit coupling (SOC) only contributed ~ 0.01 cm^{-1} due to the negligible effective SOC constants of the C and N atoms.

Reactivity of triplet nitrene 2

We further explored the reactivity of **2** to better understand its chemical properties (Fig. 4). When photolysis of **1** was carried out in THF or *n*-hexane, **2** was first formed, however it decomposed rapidly to afford amine **3**, which might be formed through hydrogen abstraction from the solvent with **2**. Subjecting **2** to trimethylphosphine afforded phosphinimide **4**. Pertinent to aziridination reactions, nitrene **2** reacted with styrene to generate aziridine **5** via [1 + 2] cycloaddition, in accordance with the mechanism proposed previously.[47]

Conclusion

Since the first proposal of nitrene species as reaction intermediates that put forward more than 130 years ago, we finally succeeded in isolating and unambiguously characterizing a thermally stable triplet nitrene. The high stability is attributed to the steric shielding of the reactive monovalent nitrogen atom, as well as the effective electron delocalization endowed by the supporting hydrindacene ligand. Isolated nitrene reacts with PMe_3 to afford phosphinimide and undergoes an aziridination reaction with styrene. This work not only presents a long-sought reaction intermediate, but also provides in-depth insights into the reaction mechanisms involving nitrenes.

Declarations

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Data availability: All data are available in the main text or the supplementary materials Details about the materials and methods, experimental procedures, characterization data, and NMR spectra are available in the Supplementary Information. The structures of **1**–**6** in the solid state were determined by SC-XRD analysis and the crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under nos. CCDC 2354664 (**1**), 2354665 (**2**), 2354666 (**3**), 2354667 (**4**), and 2354668 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Author contributions: G.T., and S.Y. conceived and supervised the project, and procured the funding. D.W., H.C. and Y.C. carried out the experiments. W.C. performed the electronic structure studies. D.W., W.C. and H.C. contributed equally to the work.

Competing interests: The authors declare no competing interests.

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Figures

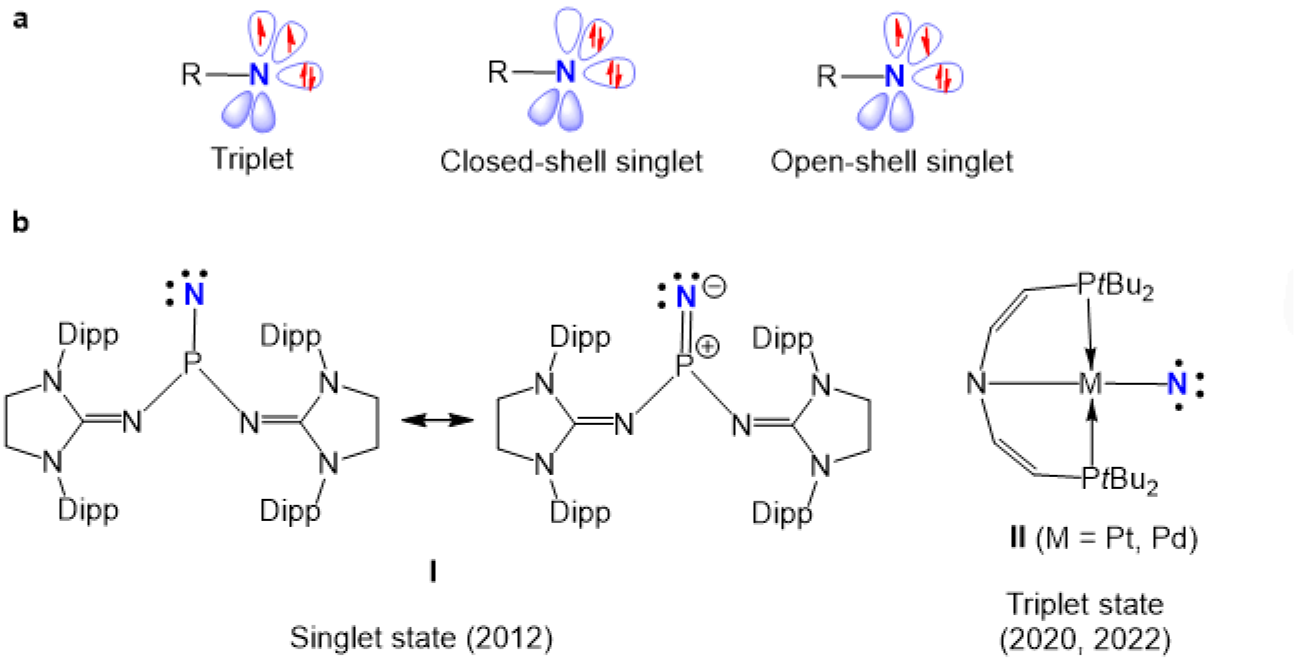

Figure 1

Electronic structures and structurally characterized nitrenes. (a) Depiction of the electronic configurations of free nitrenes. (b) Isolable singlet nitrene I supported by a bis(imino)phosphino ligand obtained by Bertrand and coworkers; the photocrystallographic method generated triplet platinum-substituted nitrene **II**, as reported by the group of Schneider. Dipp, 2,6-bis(isopropyl)phenyl; *t*Bu, tertbutyl.

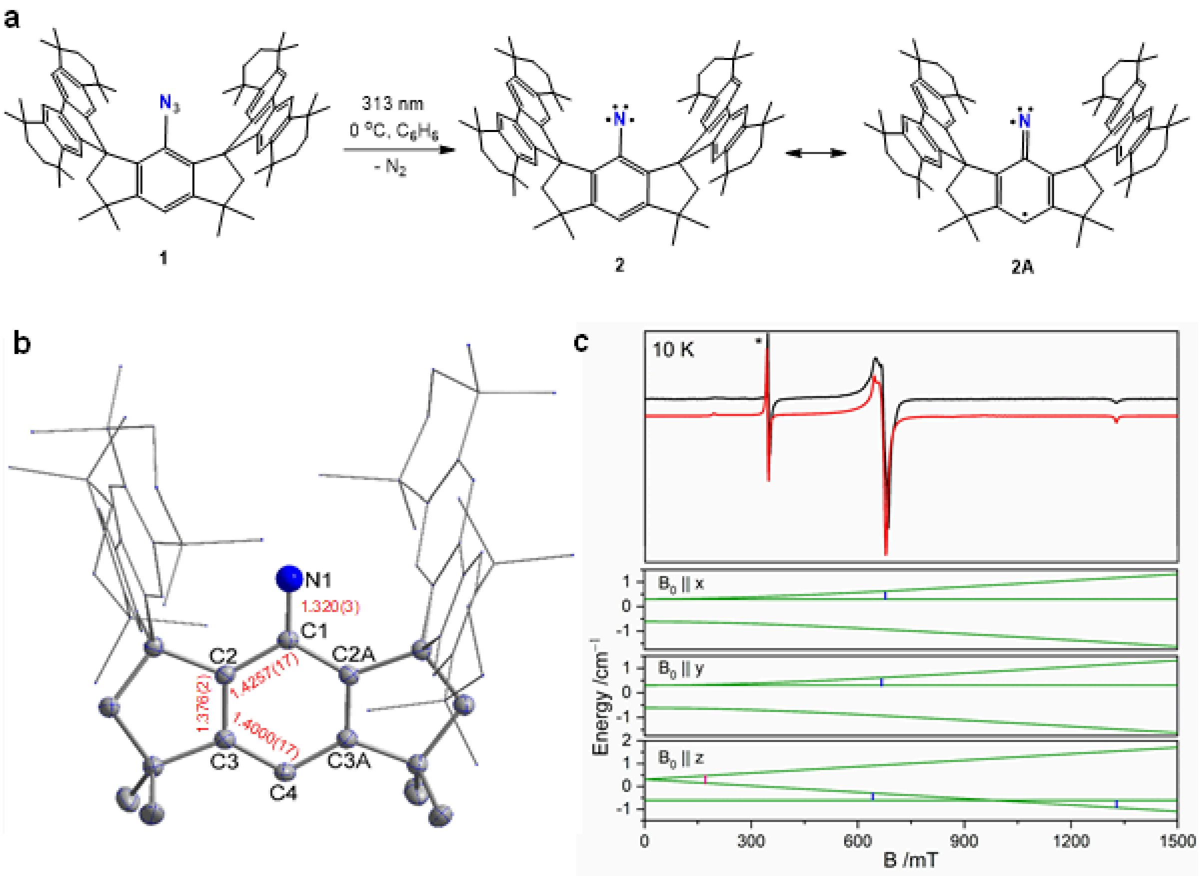

Figure 2

Synthesis and characterization of 2. (a) UV irradiation of azide **1** in benzene solution at 0 °C to afford free nitrene **2**. Resonance structure **2A** contributes considerably to the ground-state electronic structure. (b) Thermal ellipsoids of the molecular structures of **2** depicted at 50% probability; the flanking fluorenyl moieties are shown in a wireframe style, and hydrogen atoms are omitted for clarity. The red numbers show the bond lengths in Ångstrom. Atoms labeled with ‘A’ are generated by an operator of symmetry: 3/2-X, +Y, 1-Z. (c) Top: X-band EPR spectrum (black line) of a powder sample of **2** recorded at 10 K. Simulation parameters (red line): $S = 1$, $g_{iso} = 2.00$, $D = 0.92$ cm^{-1}, and $E/D = 0.002$. Bottom: Calculated energy variations of $S = 1$ levels (green lines) with the parameters given above as a function of the external magnetic field. The vertical blue and red lines represent allowed and forbidden EPR-transitions, respectively. * denotes trace $S = 1/2$ paramagnetic impurities that account for < 1% of the total intensity.

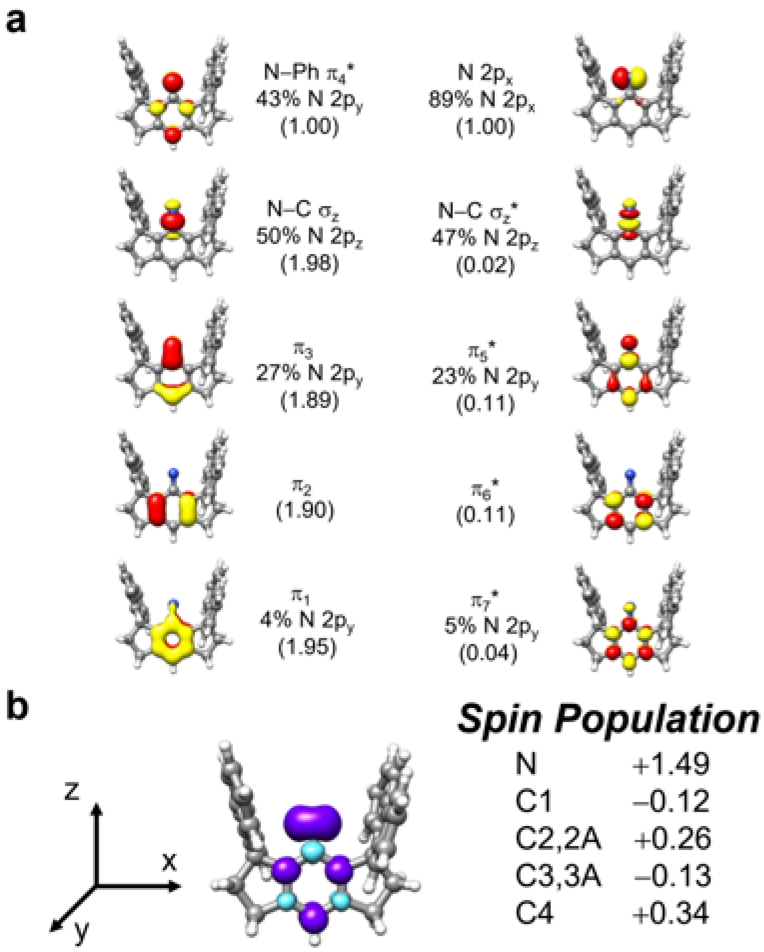

Figure 3

Electronic structure of 2. (a) Natural orbitals obtained from CASSCF(10,10) calculations of the ground state. The occupation number of each orbital is shown below the orbital label and the N atomic contribution to each molecular orbital is shown. (b) Computed spin density and atomic contributions thereof.

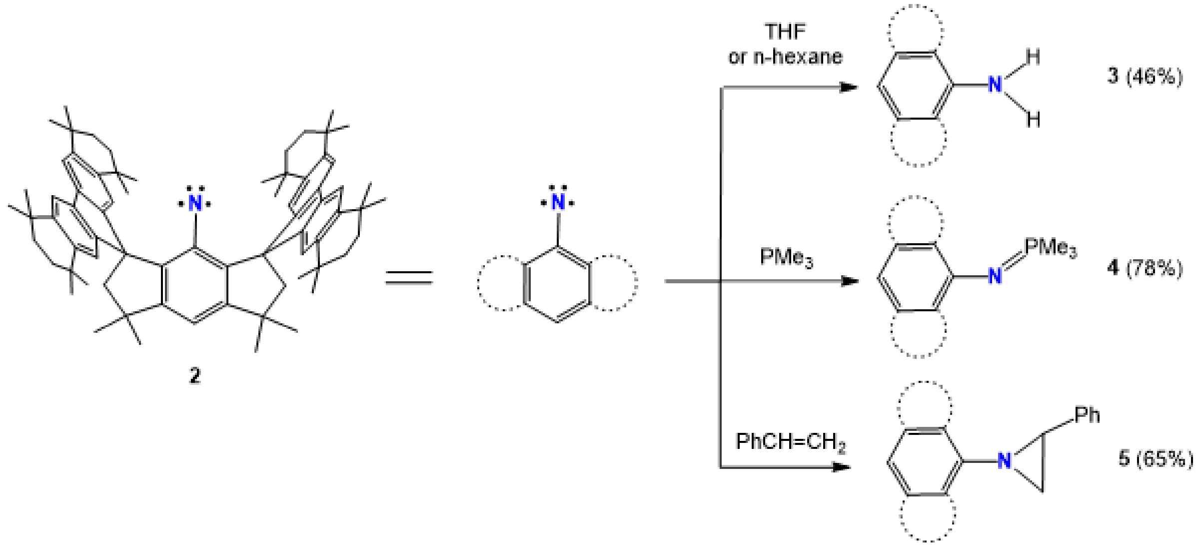

Figure 4

Reactivity studies of nitrene 2. 2 decomposed rapidly in THF and n-hexane to afford amine **3**. Phosphinimide **4** is formed in the reaction of **2** and trimethylphosphine. **2** undergoes [1+2] cycloaddition with styrene to afford aziridine **5**.

Supplementary Files

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