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Synthesis and structural characterization of a C_4 cumulene including 4-pyridylidene units, and its reactivity towards ammonia-borane†

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A novel type of C_4 cumulene derivative featuring 4-pyridylidene units has been synthesized. X-ray diffraction analysis revealed the presence of consecutive C═C double bonds in the C_4 backbone as well as the quinoidal pyridylidene structure. This C_4 cumulene derivative readily reacted with ammonia-borane, which resulted in transfer hydrogenation of the central C═C double bond.

Over the last couple of years, various compounds featuring main group elements in the zero oxidation state have been synthesized by taking advantage of stabilization ability of singlet carbene ligands.[1,2] Bertrand and Frenking *et al.* reported a series of carbene-stabilized carbon(0) species displaying ylidone properties (L:→:C:←:L), termed also bent-allenes.[3] More recently, Roesky and Bertrand *et al.* independently isolated C_4 cumulene derivatives **I–II**[4,5] that can be viewed as diatomic carbon $[C_2]$ supported by two cyclic(alkyl)(amino)carbenes (CAACs) (Fig. 1).[6] In their reports, it has also been demonstrated that CAAC ligands can not only stabilize the cation radical $[C_2]^{\bullet+}$ which afforded air stable organic mixed valence species $[(CAAC)_2C_2]^{\bullet+}$, but also dicationic species $[C_2]^{2+}$. The successful synthesis of these unique species relied on the stronger nucleophilic and electrophilic properties of CAACs with respect to N-heterocyclic carbenes (NHCs).[7]

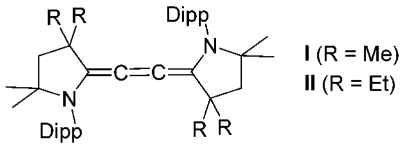

Fig. 1 C_4 cumulene derivatives including CAACs **I** and **II**.

Recently, various types of carbene ligands other than NHCs have been reported.[7] Among them, pyridylidenes that are isomers of pyridines with a carbene carbon in the 6-membered ring with 6π-electrons[8] are found to be more σ-donating and π-accepting ligands due to their higher HOMO and lower LUMO compared to NHCs or even CAACs.[9] We were curious to introduce pyridylidenes into a C_4 cumulene system to extend the C_4 cumulene family. In particular, investigation of the interaction between the 6π-electrons of pyridylidenes and a C_2 fragment would be significant from both fundamental and application points of view. Here, we report the preparation, single crystal X-ray diffraction, and computational studies of a cumulene derivative containing 4-pyridylidene units. We also describe its reactivity towards ammonia-borane.

Since isolable pyridylidenes are not available, we decided to construct 4-pyridylidene by N-alkylation of pyridine groups attached to the sp-carbon atoms of alkynes in the course of the synthesis. Dicationic alkyne **6** was synthesized *via* five steps from 4-chloro-3-mesityl pyridine **1** (Scheme 1). Thus, treatment of **1** with excess amounts of sodium iodide gave 4-iodo-3-mesityl pyridine **2** (55%), which was coupled with trimethylsilyl acetylene by Sonogashira coupling to afford **3** in 53% yield. Then, a cross-coupling reaction between **2** and **4** which was generated by reaction of **3** with potassium dicarbonate afforded **5** (42%) which was fully characterized by NMR spectroscopy and X-ray diffraction analysis. N-methylation of **5** with two equivalents of methyl trifluoromethanesulfonate in dichloromethane afforded **6** in 80% yield. Next, we performed the reduction of **6**. Treatment of dicationic alkyne **6** with two equivalents of potassium graphite in THF immediately afforded a deep purple solution. After work-up, the desired C_4 cumulene **7** was obtained as a black solid in 60% yield. Note that **6** and **7** can be viewed as $[C_2]^{2+}$ and $[C_2]$ fragments, respectively, supported by two 4-pyridylidenes.[10] In the ^{13}C-NMR spectra of **7**, a signal appeared at 104.6 ppm corresponding to the central sp-hybrid carbons, which shifted downfield with respect to that (71.2 ppm) of **I**[4] but upfield compared to that (127.9 ppm) of **II**.[5] Compound **7** is thermally stable both in the solid state and in solution at ambient temperature but it gradually decomposes upon exposure to air. Single crystals of **7** were obtained from a

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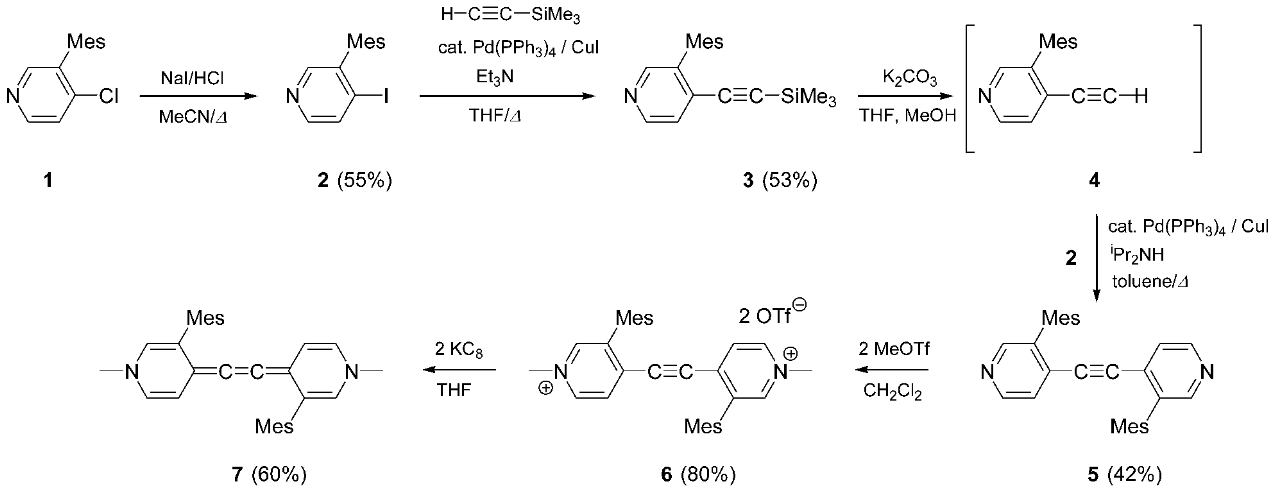


Scheme 1 Synthesis of **7** (Mes = 2,4,6-trimethylphenyl).

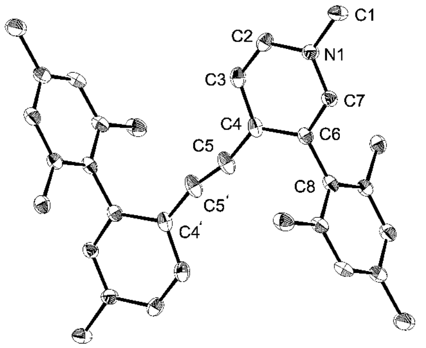


Fig. 2 ORTEP drawing of **7**, all hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°]; values calculated at the M05-2X/6-311G(d,p) level of theory are given in square brackets: C5–C5′ 1.207(8) [1.251], C4–C5 1.371(5) [1.341], C2–C3 1.338(5) [1.344], C3–C4 1.442(6) [1.453], C4–C6 1.467(5) [1.463], C6–C7 1.355(5) [1.347], C6–C8 1.486(5) [1.488], C4–C5–C5′ 165.8(7) [179.4], C3–C4–C5 120.9(4) [123.1], C3–C4–C6 115.1(3) [115.1], C5–C4–C6 123.9(4) [121.8].

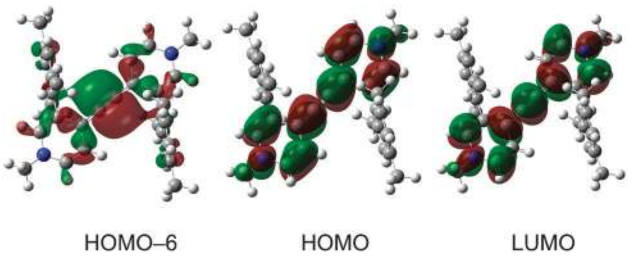


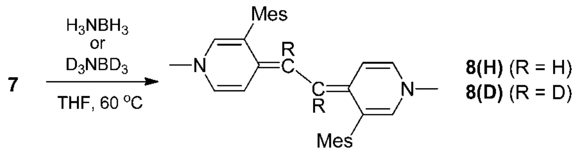
Fig. 3 Plots of molecular orbitals of **7**.

concentrated solution of THF at room temperature, and the solid state structure was characterized by X-ray diffraction analysis (Fig. 2).

The geometry of 7 displays C_2-symmetry and two six-membered N-heterocyclic rings are nearly co-planar with trigonal planar geometries around the N atoms (the sum of bond angles = 359.8°). The C_4 backbone deviates from linearity (C4–C5–C5′ 165.8(7)°), which is more acute than those (177.73(16) and 178.82(15)°) observed in **I** and **II**. The C_4 backbone has consecutive C═C double bonds, and the bond length of C5–C5′ (1.207(8) Å) is shorter than those (1.249(2) Å and 1.266(2) Å) of **I** and **II** whereas the C4–C5 bond length of 1.371(5) Å is slightly longer than those (1.3236(16) Å and 1.3332(17) Å) in **I** and **II**. The N-heterocyclic rings show significant C–C bond alterations. The bond distances of C2–C3 (1.338(5) Å) and C6–C7 (1.355(5) Å) are shorter than those of C3–C4 (1.442(6) Å) and C4–C6 (1.467(5) Å) bonds, which corresponds to the quinoidal pyridylidene structure. The theoretically optimized geometry of 7 is essentially in agreement with experimental structural parameters (Fig. 2),[11] except for a difference in the C4–C5–C5′ bond angle [exp. 165.8(7)°, calcd 179.4°], which is presumably due to the crystal packing force.

To gain further insight into the electronic feature of 7, we performed quantum chemical calculations at the M05-2X level of theory with the 6-311G(d,p) basis set.[11] The HOMO − 6 of 7 presents in-plane π-bonding orbital at the central C_2 fragment (Fig. 3, left). The HOMO is the π*-orbital of the central C_2 fragment, which mixes in a bonding fashion with p(π) AOs of the C4 carbons in the pyridylidene rings (Fig. 3, center). Note that the HOMO − 6 and HOMO are perpendicular to each other. Meanwhile, the LUMO corresponds to the π-orbital of the central C_2 fragment, which exhibits antibonding conjugation with the π-system of the pyridylidene rings at C4 (Fig. 3, right). Natural bond order (NBO) analysis gave the Wiberg bond index (WBI) value for the central C5′–C5 bond (2.16), which is consistent with the short C5′–C5 bond distance. WBI for the C4–C5 bond (1.51) indicates a strong interaction between the C_2 fragment and two pyridylidene ligands. Indeed, natural population analysis (NPA) revealed an almost neutral charge (−0.08) at the C_2 fragment, which is in line with the charge exchange that formally occurs *via* pyridylidenes → C_2 σ-donations and C_2 → pyridylidene π-back donations.

Recent breakthroughs in the use of p-block elements as mimics for transition metals demonstrate that a variety of main group compounds can activate small molecules and enthalpically strong bonds.[12] There are a few reports on the activation of



Scheme 2 Reactions of **7** with H_3NBH_3 or D_3NBD_3.

B–H and N–H bonds of ammonia-borane **AB** by main group molecules.[13] Because **AB** has a high gravimetric hydrogen density (19.6 wt%), it has attracted great interest recently.[14] To achieve the potential application of **AB** as a H_2 storage material, studies on a process to activate B–H and N–H bonds of **AB** are essential. Therefore, next we were interested in the reactivity of **7** towards **AB**. A THF solution of **7** with two equivalents of **AB** was stirred at 60 °C for 1 h. After removing the solvent *in vacuo* and work-up, **8(H)** was obtained as a black powder in 50% yield (Scheme 2). The ^{1}H-NMR spectra of **8(H)** display a signal at 4.47 ppm, which corresponds to the protons at the central sp^2-hybrid carbons. In the ^{13}C-NMR spectrum of **8(H)**, the central sp^2-carbon appears at 101.9 ppm. In order to confirm the source of the hydrogen atoms on the central carbon atoms in **8(H)**, the same reaction employing deuterated-**AB** (D_3NBD_3) was performed.[15] After the reaction, the clean formation of **8(D)** was observed upon the disappearance of the proton peak corresponding to the central C*H* in **8(H)**, demonstrating that **8(H)** was formed *via* activation of both B–H and N–H bonds by **7**. This reaction can also be considered as the first example of transfer hydrogenation of cumulene or the C_2 fragment with **AB**.[16] Note that, although there are examples of metal-free transfer hydrogenation from **AB** to unsaturated bonds[17] such as imines (C═N), ketones (C═O), and highly polarized alkenes (C═C), transfer hydrogenation of non-polar carbon–carbon double bond has never been described thus far. According to the theoretical calculation result on **AB** (see the Supporting Information), the energy gap (ΔE = 5.63 eV) between the HOMO of **7** and the LUMO of **AB** is much smaller than that (ΔE = 9.21 eV) between the LUMO of **7** and the HOMO of **AB**. Thus, the initial step in this reaction may involve the deprotonation of a hydrogen atom on the N atom of **AB** by **7** (Fig. 4a) rather than the migration of a hydride from the B atom of **AB** to **7** (Fig. 4b). However, a concerted double hydrogen transfer process *via* a six-membered ring transition state[13a,17d,18] cannot be ruled out as both interactions are essentially orbital symmetry-allowed.

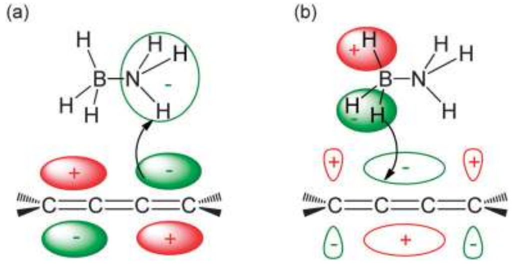


Fig. 4 Orbital interactions between **7** and **AB**; (a) the HOMO of **7** and the LUMO of **AB**; (b) the HOMO of **AB** and the LUMO of **7**.

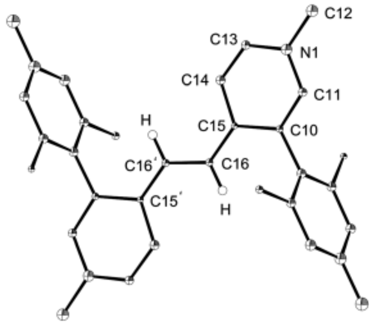


Fig. 5 ORTEP drawing of **8(H)**, all hydrogen atoms except for those on the central C_2 fragment are omitted for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°]: C16–C16′ 1.411(3), C15–C16 1.378(2), C13–C14 1.345(3), C14–C15 1.449(2), C10–C11 1.352(2), C10–C15 1.460(2), C15–C16–C16′ 127.2(2), C14–C15–C16 123.88(16), C10–C15–C16 122.76(16), C10–C15–C14 113.34(15).

Compound **8** is thermally stable both in the solid state and in solution, and even under heating at 110 °C for several hours in toluene, no decomposition was detected. However, it rapidly decomposed upon exposure to air or moisture. Recrystallization from a THF solution of **8(H)** at room temperature under argon afforded single crystals, and the solid-state structure of **8(H)** was confirmed by X-ray diffraction study (Fig. 5). The geometry of **8(H)** shows C_2-symmetry with cisoid (*s-cis*) conformation, and two six-membered N-heterocyclic rings are nearly co-planar. The bond length of C16–C16′ (1.411(3) Å) is in the range of the typical C–C single bond length, and significantly longer than the corresponding central C–C bond (1.207(8) Å) in **7**. In contrast, the C15–C16 bond length of 1.378(2) Å is nearly identical to that (1.371(5) Å) in **7**. C–C bond alteration was observed in the six-membered N-heterocyclic rings; thus, the bond distances of C10–C11 (1.352(2) Å) and C13–C14 (1.345(3) Å) are shorter than those of C14–C15 (1.449(2) Å) and C10–C15 (1.460(2) Å) bonds, which is in line with the quinoidal pyridylidene structure.

In summary, we synthesized a novel type of C_4 cumulene derivative **7** involving 4-pyridylidene units. X-ray diffraction analysis and computational studies revealed the unique bonding situation and the electronic properties of **7**; thus, the 6π-system of pyridylidenes possessing the quinoidal structure is conjugated through the C_2 fragment. Compound **7** readily reacted with ammonia borane at 60 °C, and activated the B–H and N–H bonds which afforded **8(H)** quantitatively. We are currently exploring the further reactivity of **7**.[19]

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19 Although we have examined the reactions of **7** with H_2, NH_3, diphenyl acetylene, and PhN$=$CHPh, no reactions were observed for all of them, even under heating conditions (~90 °C).