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Communication

Mesoionic Carbenes

Isolation and Structures of 1,2,3-Triazole-Derived Mesoionic Biscarbenes with Bulky Aromatic Groups

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Abstract: 1,2,3-Triazole-derived mesoionic biscarbenes bridged by a pyridylene group were synthesized and their structures were determined. Bulky substituents on the carbene rings stabilized the carbenes, which enabled their crystal structures to be determined. As implied by DFT calculations and the experimental results, the carbenes are partly reduced to anionic radical species in the presence of strong bases. This suggests that the pyridylene and triazolylidene moieties endow molecules with both electron-acceptor and -donor properties. A rare example of an iron complex with a pincer carbene was synthesized.

Introduction

The chemistry of stable carbenes has been widely studied in both organic and inorganic chemistry.[1] Such compounds are used as organic catalysts on the basis of their strongly basic properties for organic synthesis[2] and as ligands for the construction of metal complexes for catalysts or other functional materials.[3] The singlet electron pair can be stabilized by heteroatoms adjacent to the carbene carbon atom and by the introduction of large substituents around it.[1] Various stable carbene core structures are known, including the familiar N-heterocyclic carbenes (NHCs) and mesoionic carbenes (MICs), in which the heteroatom positions are different from those in NHCs (Figure 1).[4]

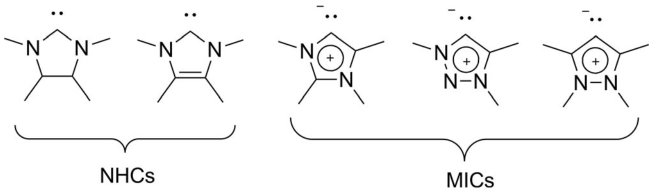

Figure 1. Representative examples of NHCs and MICs.

Various MICs have been developed and used as new alternatives to NHCs as strong σ-donor ligands in metal complexes.[4] Bertrand et al. first reported a 1,2,3-triazole-derived MIC (triazolylidene) ligand.[5] MICs have been attracting increasing attention, because a click reaction, that is, the copper-catalyzed [2+3] Huisgen cycloaddition to form 1,2,3-triazoles,[6] makes this ligand easier to synthesize than other carbene ligands. The σ donation by a 1,2,3-triazole-derived carbene to metals is stronger than that by common NHCs.[5] Many metal compounds containing various triazolylidene ligands have been reported.[7]

Several synthetic pathways to MIC complexes have been reported.[7] However, tridentate bisMICs have not been isolated, although a silver-stabilized carbene was reported as an intermediate in the synthesis of a series of luminescent ruthenium complexes by Schubert et al.[8] Bertrand et al. reported the structure of a potassium-stabilized tridentate MIC.[9] In this paper, we report the first isolation of free tridentate carbenes and an iron complex. Schubert's sequential method was used to synthesize the carbenes, as shown in Scheme 1. Furthermore, we were interested in the effects of a pyridine moiety placed between two triazolylidene moieties. In conjunction with the pyridine ring directly bound to the triazolylidene moieties, this type of molecule could have specific electronic properties derived from extended π conjugation, which cannot be observed in monodentate carbene molecules. The experimental and theoretical results and a discussion concerning the expanded π conjugation in such free carbene molecules have not been reported to the best of our knowledge.

Results and Discussion

A [2+3] Huisgen cyclization by using 2,6-bisethynylpyridine and an aryl azide afforded 1,2,3-triazoles **1a** (Ar = 2,6-diisopropylphenyl) and **1b** (Ar = 2,4,6-trimethylphenyl) in high yields (Scheme 1). Triazolium salts **2a** and **2b** were obtained by reactions of **1a** and **1b** with trimethyloxonium tetrafluoroborate. The obtained triazolium salts contained tetrafluoroborate anions. Desired carbenes **3a** and **3b** were synthesized from **2a** and **2b** with sodium *tert*-butoxide at room temperature; the products were obtained after filtration through Celite. The solvents used for carbene preparation were critical in terms of efficient formation and isolation of the products. Ether was the best solvent for the reduction. The carbene molecules were stable in toluene, and therefore, the reaction mixtures were extracted with toluene and filtered through Celite after removal of ether from the reaction mixture. These results were encour-

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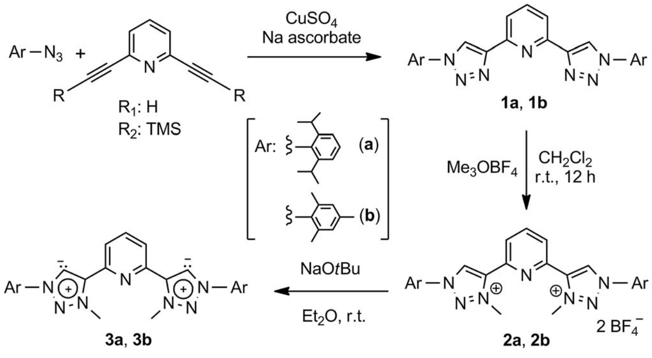
aging, because it has been reported that potassium *tert*-butoxide and bis(trimethylsilyl)amide generally reduce triazolium salts with up to moderate conversions.[4]



Scheme 1. Synthesis of MICs **3a** and **3b**.

Compound **2a** was identified by using common spectroscopic methods (see the Supporting Information); it is similar to **2b**, which was previously reported.[8] In the ^1H NMR spectra of **3a** and **3b**, the signals from the methyl protons on the triazole nitrogen atom appear at δ = 3.77 and 3.75 ppm, respectively. The doublet signals from the methyl protons of the isopropyl groups in **3a** are split into two signals (δ = 1.30 and 1.22 ppm), which indicates that free rotation of the aromatic ring on the triazolylidene moiety is restricted because of steric repulsion between the triazole ring and the isopropyl groups at the 2,6-positions (see the Supporting Information). The ^{13}C resonances from the carbene carbon atoms in **3a** and **3b** are observed at δ = 206.78 and 201.54 ppm, respectively; these are higher than the resonance of an NHC analogue, which appears at δ = 219 ppm.[10] These values are comparable to those of other triazolylidenes, which confirmed triazolylidene formation.[11]

A single crystal of **3a** suitable for X-ray crystallography was obtained from a toluene/*n*-hexane (5:1) solution at –30 °C.[12] Figure 2 shows the structure of **3a**. This is the first example of a crystal structure of a free tridentate mesoionic carbene. The three directly connected central rings are mainly located in the same plane, although one of the triazole rings is slightly twisted [the torsion angle N1–C5–C8–N7 is 16.8(4)°] because of steric repulsion between the methyl groups on the triazole nitrogen atom. This is in contrast to the two NHC and pyridine rings of the bisNHC analogue, which has no methyl groups; the crystal structure shows that the rings are in the same plane.[10] The C–C bond lengths between the three central rings C1–C6 and C5–C8 are 1.475(4) and 1.476(4) Å, respectively. These bonds are about 0.06 Å shorter than a C–C single bond, which supports the existence of extended π conjugation. The 2,6-diisopropylphenyl groups on the triazole rings are twisted perpendicularly from the three central rings, as suggested by the ^1H NMR spectrum. Similar to the reported triazolylidene, the five-membered ring has a conjugated structure:[5,11] the five bond lengths of one of the triazolylidene rings, N2–N3, N3–N4, N4–C6, C6–C7, and C7–N2 are 1.350(4), 1.329(4), 1.370(4), 1.411(4), and 1.368(4) Å, respectively. The carbene carbon atom angles, C6–C7–N2 and C8–C9–N5, are 99.6(3) and 99.7(3), respectively; these are smaller than those of the NHC analogue, which are 101.1(3).[10] The smaller carbene carbon atom angles in **3a** suggest that the σ-donor ability of the triazolylidene is stronger than that of an NHC, as expected.[7a,7b]

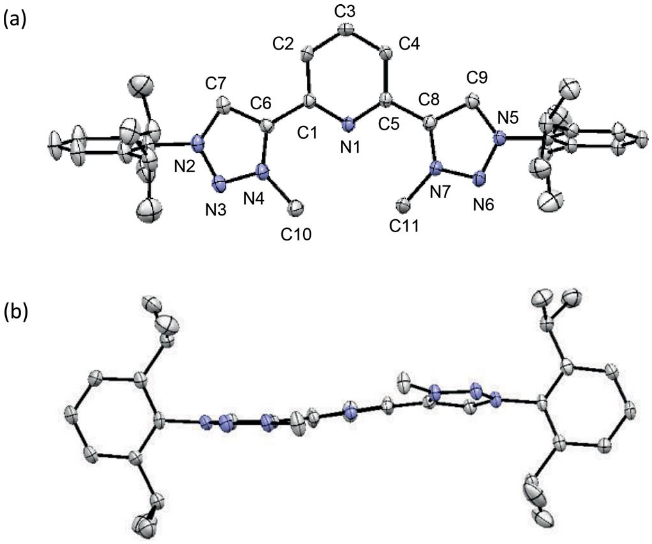


Figure 2. ORTEP diagrams of **3a** (thermal ellipsoid probability 50 %): (a) side view and (b) bottom view. Two molecules of cocrystallized toluene (used as the solvent) and hydrogen atoms are omitted for clarity.

A density functional theory (DFT) calculation with use of the B3LYP functional and the 6-31G(d) basis set suggests easy one-electron reduction of **3a**. Reduced anionic analogue **3a′** is –10.39 kcal mol^{-1} more stable than its neutral counterpart **3a** on the basis of DFT calculations. A *t*BuO$^-$ anion and solvent are proposed as possibilities of reductants to generate **3a′** as follows:

3a + *t*BuO$^-$ + toluene → **3a′** + *t*BuOH + benzyl radical

Here, charge transfer from the *t*BuO$^-$ anion to **3a** gives rise to **3a′** and the *t*BuO$^\cdot$ radical, which promptly abstracts a hydrogen atom from the toluene solvent to give a benzyl radical. This reaction energy was calculated to be +3.67 kcal mol^{-1}, and consequently, this reaction equilibrium sufficiently provides **3a′** at room temperature.

The singly occupied molecular orbital (SOMO) of radical anion **3a′** calculated by DFT calculations also showed predominant single-electron distribution in the delocalized π^* orbitals of pyridylene and both triazolylidenes (Figure 3). Because of its stability, **3a** could easily accept a single-electron transfer from

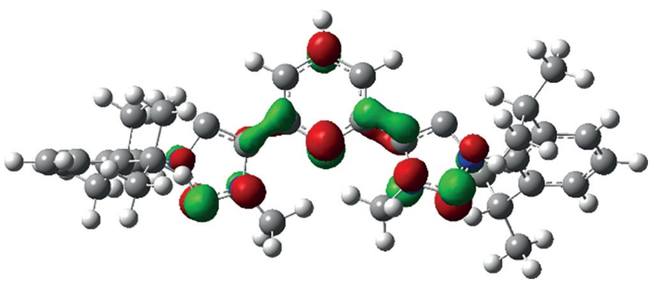
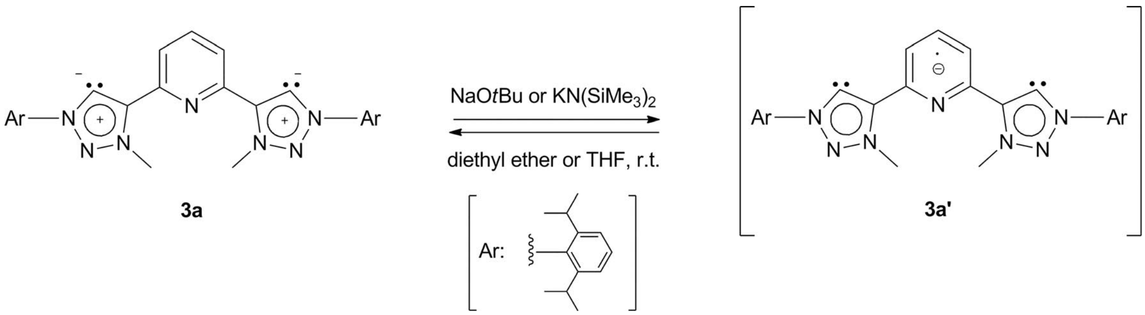


Figure 3. SOMO of **3a′** obtained by DFT calculations at the B3LYP/6-31G(d) level.



Scheme 2. Formation of a possible radical anion of MIC **3a**.

the reductant. Although the formation of the radical anion of pyridine derivatives has been reported,[13] the radical anion of pyridylene between two N-heterocyclic carbenes is not known to the best of our knowledge.

Supporting these calculation results, we found experimental evidence of an anionic radical species of **3a**. Products **3a** and **3b** were dark purple after filtration through Celite, whereas their crystals were colorless. No color change was noted in the preparative process of the reported NHC analogue.[10] The ^{1}H NMR spectrum of product **3a** shows that prominent signals from byproducts cannot be detected, and only signals of **3a** and those of an excess amount of reductant are observed (see the Supporting Information). We suspect that in the presence of an excess amount of a strong base such as potassium or sodium *tert*-butoxide and bis(trimethylsilyl)amide, the molecule is reduced to form radical anion **3a′** in part (Scheme 2). The radical nature of **3a′** was confirmed by using solid-state electron paramagnetic resonance (EPR) spectroscopy at room temperature. A single band was observed at $g = 2.005$ (Figure 4, a)[13] by using the solid of the dark purple product after filtration. The electronic spectrum of a THF solution of the product showed broad absorption bands at around $\lambda = 400$ and 750 nm (shoulders), as shown in Figure 4 (b). The UV absorption band at around $\lambda = 400$ nm and a near-IR band at $\lambda = 750$ nm is consistent with the simulated electronic transition spectrum of an anionic isomer of **3a** (see the Supporting Information). An alkali-metal-coordinated anion radical complex[9] is also possible, because the stabilization energy by coordination with metal cations was comparable to that of the free anion radical, according to the calculations. Other possibilities such as the generation of triazolylidene-to-pyridine charge transfer induced by the positive metal center can be ruled out on the basis of the calculations. The resulting radical species generated from the reductant cannot be detected, probably because of facile radical trap by the solvent molecules. These findings suggest that the heteroaromatic rings in **3a** are potential electron acceptors, although both MICs are strong donors as ligands.

The pyridylene-bridged biscarbene can stabilize an iron complex.[14] The above results prompted us to use a tridentate pincer-type ligand to form an iron complex, because there has only been one reported example of a triazolylidene ligand bound to iron.[15] The room-temperature reaction of in situ generated triazolylidene **3b** with iron(II) chloride in THF/ether afforded a dark purple solution at room temperature. Ammonium hexafluorophosphate was added to the solution as an anion-exchange reagent to stabilize the compound (36 % conversion from carbene). Unfortunately, the purification procedure, alumina column chromatography and subsequent recrystallization, diminished the yield of the product (2 % yield). MS (ESI) in acetonitrile solution showed the generation of dicationic iron complex **4** bearing two triazolylidene ligands (Scheme 3). The ^{1}H NMR spectrum of **4**-PF$_6$ indicated that the compound is diamagnetic. Single-crystal X-ray crystallography showed that complex **4** has octahedral geometry around the iron(II) center.[12,16]

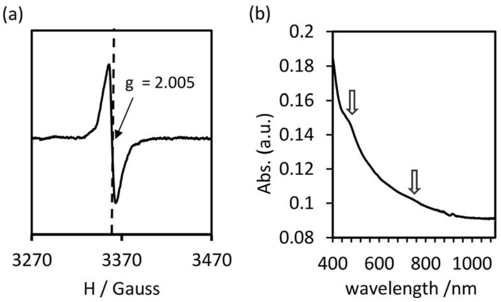
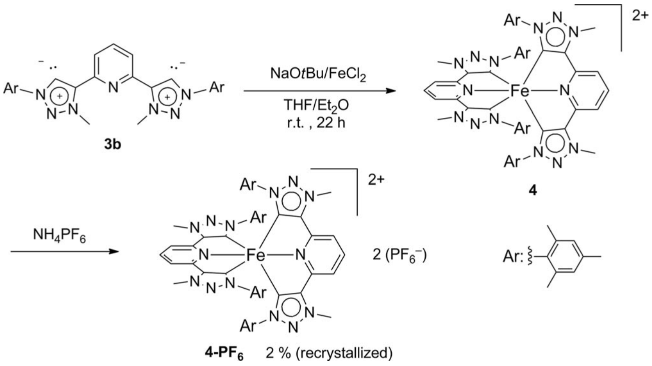


Figure 4. (a) EPR spectrum of a mixture of **3a** and **3a′** in the solid state at room temperature and (b) the UV/Vis spectrum of the same mixture in THF.



Scheme 3. Reaction of **3a** with iron(II) chloride.

Conclusions

In summary, 1,2,3-triazole-derived biscarbenes were synthesized. The two carbene groups were bound to the central pyridylene and had bulky 2,6-diisopropylphenyl or 2,4,6-trimethylphenyl groups. The biscarbenes were characterized by NMR spectroscopy and their structures were confirmed by X-ray crystallography. Theoretical calculations showed that one-electron reduction of the molecule is energetically possible, and this is indicative of amphoteric compounds with both electron-donor and electron-acceptor properties. That was supported by the electron paramagnetic and electronic spectra of product **3a** in the presence of an excess amount of a strong base. A rare example of a 1,2,3-triazole-derived carbene complex of iron(II), a pincer-type cationic complex, was obtained by reaction of iron chloride with in situ generated triazolylidene **3b**. Further studies on transition-metal complexes with these carbenes for catalytic applications are ongoing.

Experimental Section

Preparation of 3a: Typically, a Schlenk tube was charged with **2a** (100 mg, 0.136 mmol), NaO*t*Bu (29.7 mg, 0.306 mmol), and diethyl ether (0.80 mL) in a glovebox. The mixture was stirred for 1 h, and then, the volatiles were removed under reduced pressure. After extraction with toluene, the solution was filtered through Celite. The solvent was removed under reduced pressure to give **3a** as a purple-white solid (71.0 mg, 80 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 8.83 (d, J = 8.0 Hz, 2 H, Py-H), 7.33 (t, J = 8.0 Hz, 2 H, Pro-Ph), 7.27 (t, J = 7.6 Hz, 1 H, Py-H), 7.21 (d, J = 8.0 Hz, 4 H, Pro-Ph), 3.77 (s, 6 H, Trz-H), 2.92 (sept, J = 7.2 Hz, 4 H, Pro-Ph), 1.30 (d, J = 6.8 Hz, 12 H, Pro-Ph), 1.22 (d, J = 6.8 Hz, 12 H, Pro-Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 206.78 (carbene), 151.37, 147.11, 145.59, 139.54, 137.60, 129.95, 124.26, 123.84, 37.79, 28.96, 24.26, 24.10 ppm. MS (ESI-TOF): m/z = 562.37 $[M + H]^+$ ($C_{35}H_{43}N_7{\cdot}H^+$ requires 562.45).

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Keywords: Carbene ligands · Pincer-type ligands · Iron · Nitrogen heterocycles · Radical ions

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[16] Before anion exchange, crystals suitable for X-ray crystallography were accidentally given. The anion was $[FeCl_3\text{-}O\text{-}FeCl_3]^{2-}$, which suggested that iron(II) chloride, $[FeCl_3(solv)]^-$, might be oxidized upon crystallization in air.

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