Organic Chemistry
Current Research

Iwasaki et al., Organic Chem Current Res 2016, 5:1
DOI: 10.4172/2161-0401.1000161

Research Article Open Access

Synthesis and Structure of Homoleptic Iron Complex Bearing Pincer-Type 1,2,3-Triazol-5-ylidene

Haruka Iwasaki, Yuji Koga and Kouki Matsubara*

Department of Chemistry, Fukuoka University, Fukuoka, Japan

Abstract

Novel iron(II) complex bearing pyridine-bridged bis(1,2,3-triazol-5-ylidene) ligand was synthesized. During many attempts to obtain the compounds, we found generation of dicationic homoleptic iron(II) complex with two tridentate ligands. Analogous monocationic complex with only one tridentate ligand, which is an unstable intermediary complex during formation of the dicationic complex was detected. Structural identification of the homoleptic dicationic product revealed that octahedral geometry stabilized the iron complex and also π-stacking interaction exists between these two tridentate ligands.

Keywords: Mesoionic carbene; 1,2,3-Triazol-5-ylidene; Iron complex; Cationic complex; X-ray crystallography; π-π Stacking interaction

Abbreviations: THF: Tetrahydrofuran; NMR: Nuclear magnetic resonance; IR: Infrared; DFT: Density functional theory

Introduction

Mesoionic carbene (MIC) as a ligand component in metal complexes is recently focused as an alternative version of N-heterocyclic carbene (NHC), which is widely developed and utilized for functional materials such as catalysis and photochemical devices in these decades [1,2]. The most interesting feature of MIC is that strong dipole moment in its five-membered ring exists in the resonance structures, compared with the classical NHC (Figure 1) [3]. Among MIC molecules, 1,2,3-triazol-5-ylidene, which is reported by Albrecht et al. [4] and isolated by Bertrand et al. [5] has a synthetic advantage toward classical NHC. The precursor compound can be easily prepared by [2+3] Hüisgen cyclization from alkyne and azide [6,7] so called 'click reaction,' enabling introduction of various substituents easily at the 1- and 4-positions of the five-membered ring to change their steric and/or electronic properties (R^1 and R^2 in Scheme 1). Moreover, stronger σ-donor ability of the carbene carbon of 1,2,3-triazol-5-ylidene than that of classical NHC was revealed by several systematic analytical studies, such as IR resonances of the corresponding metal carbonyl species and direct measurement of ^{13}C resonances due to the carbene carbons [1,2,8]. Therefore, many examples of MICs as ligands for transition metal complexes containing Pd, Ru, Rh, Ir, Ag, Au and Cu have been reported in the recent years [1-3,9-13]. These metal complexes are applied to catalysis for organic transformations and also photoelectronic devices. However, it is surprising that only four examples of MIC-containing tridentate ligand, which can stabilize pincer-type coordination to metals, are known [14-16]. Moreover, iron-MIC complexes have not been reported except only one example [17]. Iron is the most abundant metal element on the earth. Development of homogeneous catalysis using iron as the active metal center is one of the most important issues for the sustainable development of chemical production of useful organic compounds, not using rare metal resources [18]. Therefore, many chemists started development of the chemical procedure of iron catalysts [19-21]. However, it is a drawback that iron compounds usually form high-spin paramagnetic species, which are difficult to determine the structures and are unstable attributed to the unpaired electron, decreasing strength of the bonding interactions between iron atom and ligand [22]. Quite recently, we have reported synthesis and structure of pyridine-bridged 1,2,3-triazol-5-ylidene (**3a**, **3b**), which are prepared from the corresponding bis(1,2,3-triazole) (**1a**, **1b**) as the starting material, via the methylated bis(1,2,3-triazolium) salts (**2a**, **2b**). The compounds **2a** and **2b** are easily reduced to form **3a** and **3b**, respectively, in good yields (Scheme 2) [23]. They are rare examples of the isolated MIC. The X-ray crystallography and DFT calculations of **3a** indicated its characteristic amphiphilic nature; because it has an expanded π-conjugated plane including one pyridine and two carbene rings, the stabilized π*-orbital easily accept a single unpaired electron to form anionic radical species in part, despite the fact that carbene carbons are strong σ-donor [24]. Here, we successfully synthesized and determined the tridentate MIC complex of iron. Unexpectedly, even if stoichiometric amount of the carbene ligand was added to iron halides, two molecules of the carbene coordinated to form dicationic homoleptic iron complex **4** with stepwise liberation of two halide anions from iron halides.

Materials and Methods

All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and a glove box (MBraun UniLab) unless otherwise noted. THF, toluene, hexane, and benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Organic reagents used for coupling reactions were distilled just before use. The starting materials, 2,6-bisacetylpyridine [25] and 2-azido-2,6-diisopropylbenzene [26] were prepared according to the literature. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer at room temperature in $CDCl_3$ or acetonitrile-d_3. Chemical shifts (δ) were recorded in ppm from the internal standard. IR spectra were recorded in cm^{-1} on a PERKIN ELMER Spectrum Two spectrometer equipped with a universal diamond ATR. Electrospray ionization time-

---

***Corresponding author:** Kouki Matsubara, Professor, Fukuoka University Chemistry, 8-19-1, Nanakuma Fukuoka, 814-0180, Japan, Tel: +81928716631; E-mail: kmatsuba@fukuoka-u.ac.jp

Received January 07, 2016; **Accepted** January 08, 2016; **Published** January 16, 2016

Citation: Iwasaki H, Koga Y, Matsubara K (2016) Synthesis and Structure of Homoleptic Iron Complex Bearing Pincer-Type 1,2,3-Triazol-5-ylidene. Organic Chem Current Res 5: 161. doi:10.4172/2161-0401.1000161

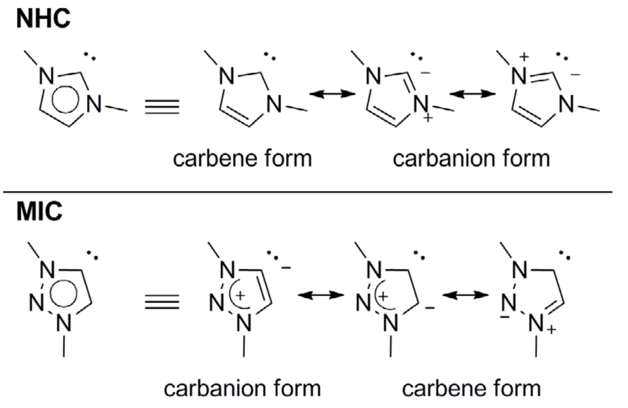
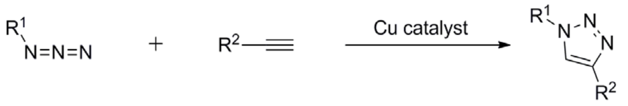
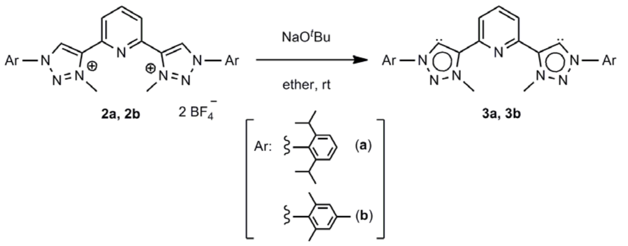


Figure 1: Resonance structures of NHC and MIC [2].



Scheme 1: [2+3] Hüisgen cyclization.



Scheme 2: Synthesis of bis(triazolylidene) **3a**, **3b** [23].

of-flight mass spectrometry (ESI-TOF MS) was carried out on a JEOL JMS-T100 mass spectrometer. The sample solutions in THF (ca. 1 μmol L^{-1}) were directly infused using THF as solvent stream. UV-visible spectra were recorded on a PERKIN ELMER Lambda 35 ES UV/VIS Spectrophotometer.

Preparation of 4b-PF$_6$

To a glass bottle were charged FeCl$_2$ (19.4 mg 0.153 mmol) and THF (11 mL) and stirred over night at room temperature. To another glass bottle were charged NaO^{t}Bu (33.5 mg, 0.349 mmol), ether (0.8 mL) and **2b** (100 mg, 0.153 mmol). The mixture was stirred for 1 h and then filtered through celite and added to the iron(II) chloride solution. The mixture was stirred for 22 h at room temperature, and then filtered through celite and NH$_4$PF$_6$ (16.9 mg 0.104 mmol) and CH$_3$CN (2.17 mL) were added and the mixture was stirred for 15 h at room temperature. After the mixture was filtered through celite, the resulting solution was removed under reduced pressure. The mixture was purified by column chromatography (alumina) eluted with CH$_3$CN and recrystallized over CH$_3$CN/THF at -30°C to give dark blue crystals (1.9 mg, 2%). ^{1}H NMR (400 MHz, CD$_3$CN) δ=7.35 (t, 2 H, *J*=8.0 Hz, Py-H), 7.08 (d, 4 H, *J*=8.0 Hz, Py-H), 6.63 (s, 8 H, *J*=8.0 Hz, MES-H), 4.41 (s, 12 H, Trz-CH$_3$), 2.22 (s, 12 H, MES-H), 1.20 (s, 24 H, MES-H); ^{13}C NMR (100 MHz, CD$_3$CN) δ=197.27 (Fe-Carbene), 152.62, 145.82, 141.76, 135.05, 134.95, 133.01, 130.08, 117.18, 39.26, 20.93, 18.39. ESI-TOF MS (m/z) 562.28, ($C_{35}H_{43}N_7 \cdot H^+$ requires 562.19).

Single-crystal X-ray diffraction study of 4b

A single crystal of **4b** suitable for X-ray diffraction study was grown at -30°C from the acetonitrile solution. The data at 110 K was collected on a Rigaku Saturn CCD diffractometer, using graphite monochromated Mo Kα radiation (λ=0.71070 Å). Data reductions of the measured reflections were carried out using the software package, Crystal Structure. The structures were solved by direct methods (SIR-2008) [27] and refined by full-matrix least-squares fitting based on F2 using the program SHELXL 2013 [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located at ideal positions and were included in the refinement, but were restricted to ride on the atom to which they were bonded. CCDC-1440830 contains the supplementary crystallographic data.

Results and Discussion

Synthesis of iron(II) complex bearing 1,2,3-triazol-5-ylidene ligand

The triazolium **2b** was reduced in the presence of sodium *tert*-butoxide in ether to form carbene in situ. Then, the resulting mixture was filtered through celite and the solution was added to THF solution of FeCl$_2$(thf)$_{1.5}$. The obtained purple solution contains iron complex **4b** as the major product (Scheme 3). NMR spectrum of the product gave broadened signals, indicating existence of paramagnetic species, probably being assignable as the counter anion FeCl$_3^-$ of **4b** and/or the resting starting iron(II) chloride (Figure 2). ESI-TOF MS spectrum showed clear peaks at 505.95 (m/z) assigned as dicationic iron species, [Fe(MIC)$_2$]$^{2+}$, calculated as ($C_{58}H_{62}N_{14}Fe$)$^{2+}$ (505.23 (m/z)) (Figure 3). The distribution of the isotopes was agreed with the theoretical one. Recrystallization of the product over acetonitrile and THF at -30ºC, purple crystals suitable for X-ray crystallography were obtained. The crystal structure of **4b** as shown in Figure 4, showed that two molecules of the tridentate ligand coordinate to cationic iron to form octahedral geometry accompanied with counter anion, (FeCl$_3$)$_2$(μ-O)$^{2-}$, which could be generated by oxidation of FeCl$_3^-$ under air. The tridentate ligands forms planar conformation without steric repulsion between methyl group in the triazole ring and C-H bond at the 3-position of pyridine, which can be anticipated in a DFT calculation of the free ligand **3a** in the previous report [23]. Averaged iron-carbon (carbene) bond distances are 1.95 Å, being smaller than those of its NHC analogue, [Fe(NHC) Br$_2$] (2.15 Å) [29]. It should be noted that π-π stacking interaction exists between the pyridine ring in one ligand and the two mesityl rings in the other ligand. The averaged distances between these rings are 3.55 Å. This interaction could stabilize coordination of the second carbene molecule. Above findings prompted us to exchange the counter anion of **4b**, (FeCl$_3$)$_2$(μ-O)$^{2-}$ or FeCl$_3^-$ with other non-metal anion, because these anions potentially disturb the NMR spectra attributed to their paramagnetic nature. According to a literature, anion was exchanged with NH$_4$PF$_6$ in acetonitrile (Scheme 4) [29]. After reprecipitation of the resulting crystalline solid in THF, small amount of dark blue crystals were obtained (2%). The ^{1}H NMR measurement of the solid in acetonitrile-*d*$_3$ revealed generation of diamagnetic compound after the anion exchange reaction, expectedly (Figure 5). That is **4b** with two PF$_6$ anions, **4b-PF$_6$**. The ^{1}H resonances due to the two carbene ligands were observed equivalently, suggesting symmetric structure around iron (II). The ^{13}C NMR spectrum also indicates its structural feature. The signal from carbene carbon was observed at 197 ppm, shifted to higher field than that from the corresponding free carbene carbon of **3b**, 201 ppm [24].

Citation: Iwasaki H, Koga Y, Matsubara K (2016) Synthesis and Structure of Homoleptic Iron Complex Bearing Pincer-Type 1,2,3-Triazol-5-ylidene. Organic Chem Current Res 5: 161. doi:10.4172/2161-0401.1000161

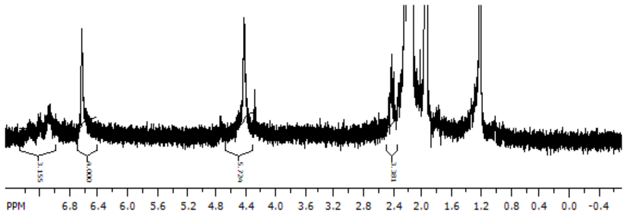


Figure 2: ^{1}H NMR spectrum of the obtained product (400 MHz, in acetonitrile-d_3).

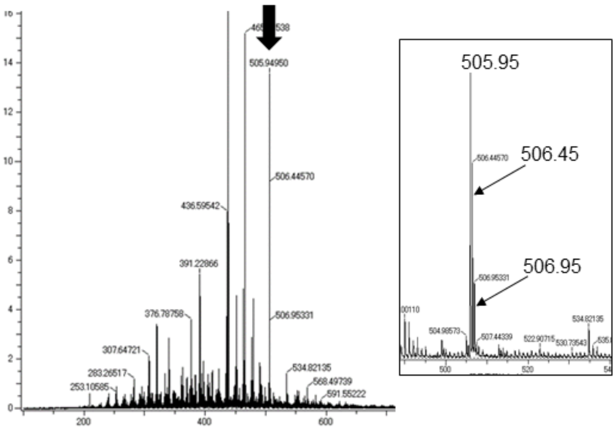


Figure 3: ESI-MS spectrum of the obtained product in acetonitrile.

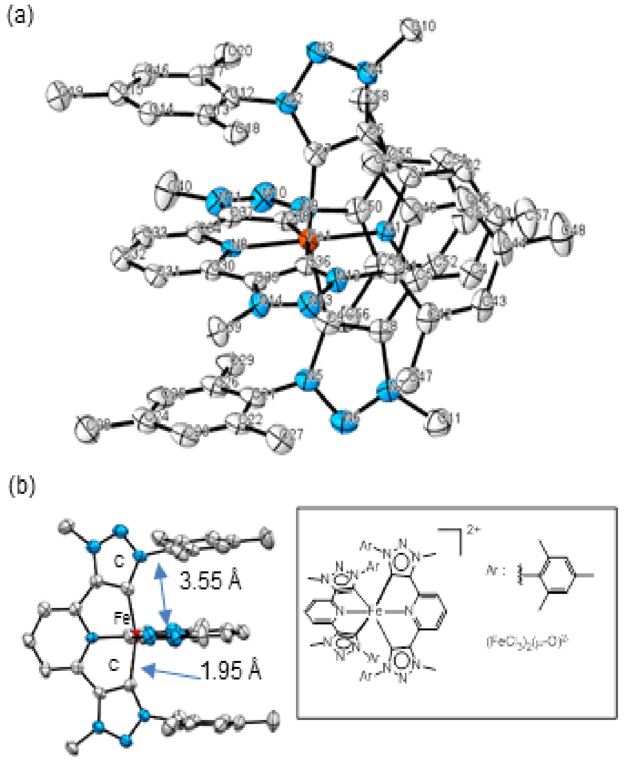


Figure 4: (a) ORTEP drawing of **4b** (50% probability of thermal ellipsoids). Hydrogen atoms, counter anion, and co-crystallized four acetonitrile molecules are omitted for clarity. (b) Averaged Fe-C$_{carbene}$ bond distance, 1.95 Å and that of π-π stacking interaction, 3.55 Å.

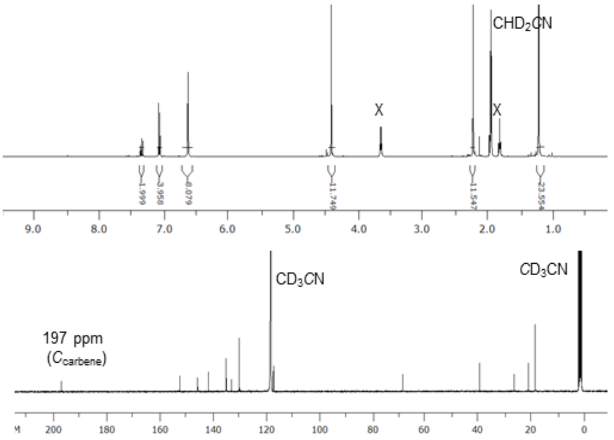


Figure 5: ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4b-PF$_6$** in CD$_3$CN (^{1}H: 400 MHz, ^{13}C: 100 MHz).

Detection of intermediary complex of iron (II) bearing one carbene ligand

The reaction of the "2,6-diisopropylphenyl" carbene analogue **3a** with an equivalent or more amount of iron(II) bromide in THF/ether solutions provided formation of a mixture containing **4a**. Monitoring the reaction mixture based on ESI-TOF MS in acetonitrile revealed that iron(II) bromide **5a** bearing only one carbene ligand was formed (Scheme 5). The mass ion peak of **5a** was observed at 696.22 (m/z), assigned as iron (II) monobromide cation, $C_{35}H_{43}N_7FeBr$ (696.21 (m/z)), in addition with that at 589.32 (m/z), assigned as the cationic part of the dicationic complex **4a** (Figure 6). Unfortunately, all of a lot of trials to isolate **5a** were in fail, because **5a** was unstable and vanished in the reaction mixture after several hours, probably giving **4a** by the reaction with excess amount of carbene and iron halide as noted below. Several solvents, such as toluene, acetonitrile, and ether did not provide selective formation of **5a**. Even though the isolated carbene molecule **3a** was used instead of in-situ generated carbene, both the MS signals due to **4a** and **5a** were observed after possible purification processes, such as filtration and/or reprecipitation.

Mechanistic considerations to form 4

Danopoulos et al. reported that two types of reactions proceeds when analogous pyridine-bridged bisNHC ligand with iron precursors [27]. (A) After reaction of the NHC ligand with iron chloride, anion exchange process with sodium tetraphenylborate ($NaBPh_4$) gives cationic iron(II) complex bearing only one NHC ligand. (B) On the other hand, that with iron(II) tetramethylethylenediamine (tmeda), $[FeCl_2(tmeda)]_2$, yields another iron complex bearing two NHC ligands (Scheme 6). In the latter reaction, they proposed that chloride anion easily eliminates from iron atom in the presence of the first NHC ligand around the iron center, inducing easy ligand exchange reaction with the second NHC ligand. Therefore, we also proposed the reaction mechanism to form **4a** from iron (II) bromide and **3a**, as follows. (1) The MIC ligand **3a** easily reacts with iron (II) bromide to form a cationic complex **3a-Fe-Br$^+$** with liberation of a bromide anion, due to strong trans effect of the MIC ligand. (2) Excess iron (II) bromide binds to bromide anion of **3a-Fe-Br$^+$** to form $FeBr_3^-$. (3) Because bromide anion consumed iron bromide to form $FeBr_3^-$, the equimolar amount of free MIC ligand **3a** was left in the reaction mixture. The carbene molecule **3a** reacts with unstable **5a** to form **4a** (Scheme 7). We also consider that the formation of **4b** also proceeds in the similar way.

Conclusions

Iron complexes bearing pyridine-bridged bis(1,2,3-triazol-5-ylidene) were synthesized. The reaction of iron(II) halides with these MIC ligands selectively form dicationic iron complexes bearing two MIC ligands. The obtained complexes were structurally determined, revealing octahedral diamagnetic geometry around iron atom. The mechanism of the formation of these dicationic complexes was proposed, indicating that easy liberation of halide anion may accelerate the ligand exchange reaction strongly supported by electron-donating MIC ligand.

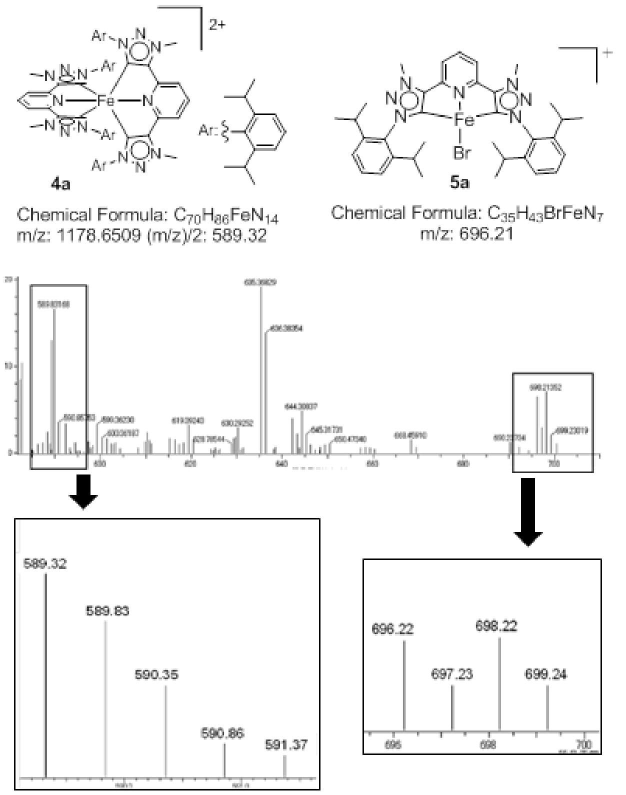
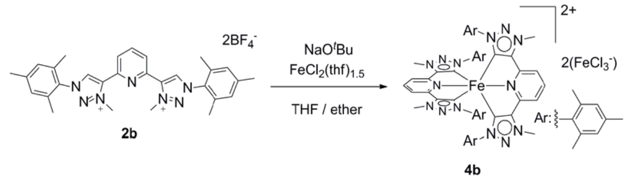
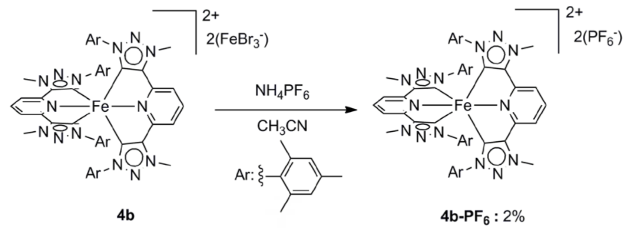


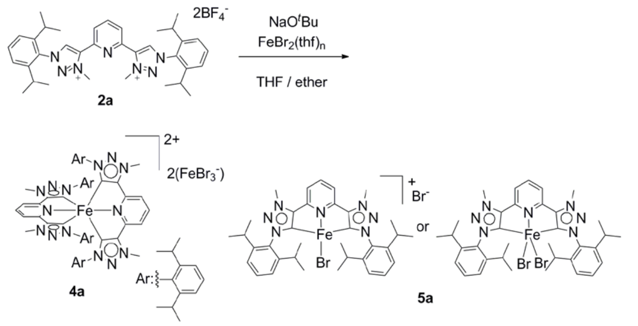
Figure 6: ESI-TOF MS spectra of the reaction mixture containing **4a** and **5a** in acetonitrile.



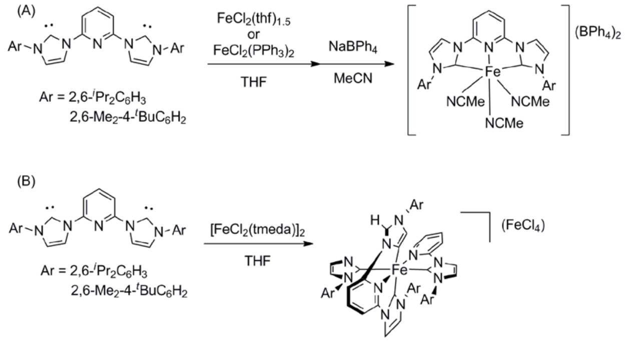
Scheme 3: Synthesis of iron MIC complex **4b**.



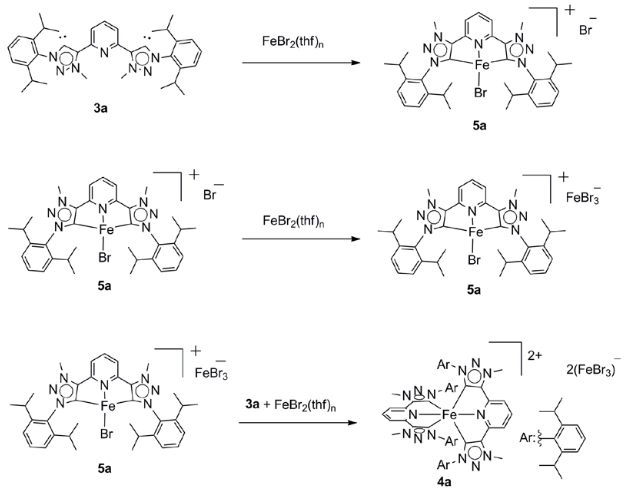
Scheme 4: Synthesis of **4b-PF$_6$**.



Scheme 5: Reaction of **2a** with iron(II) bromide.



Scheme 6: Synthesis of two types of iron complexes depending on iron precursors [19].



Scheme 7: Plausible mechanism in generation of **4a**.

Acknowledgements

This work was supported by the Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research 22550104 and 25410123) and a fund from the Central Research Institute of Fukuoka University (No. 117106).

References

1. Crabtree RH (2013) Abnormal, mesoionic and remote N-heterocyclic carbene complexes. Coord Chem Rev 257: 755-766.
2. Donnelly KF, Petronilho A, Albrecht M (2013) Application of 1,2,3-triazolylidenes

as versatile NHC-type ligands: synthesis, properties, and application in catalysis and beyond. Chem Commun (Camb) 49: 1145-1159.

3. Schulze B, Schubert US (2014) Beyond click chemistry - supramolecular interactions of 1,2,3-triazoles. Chem Soc Rev 43: 2522-2571.
4. Mathew P, Neels A, Albrecht M (2008) 1,2,3-Triazolylidenes as versatile abnormal carbene ligands for late transition metals. J Am Chem Soc 130: 13534-13535.
5. Guisado-Barrios G, Bouffard J, Donnadieu B, Bertrand G (2010) Crystalline 1H-1,2,3-triazol-5-ylidenes: new stable mesoionic carbenes (MICs). Angew Chem Int Ed Engl 49: 4759-4762.
6. Kolb HC, Finn MG, Sharpless KB (2001) Click Chemistry: Diverse Chemical Function from a Few Good Reactions. Angew Chem Int Ed Engl 40: 2004-2021.
7. Tornøe CW, Christensen C, Meldal M (2002) Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(i)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. J Org Chem 67: 3057-3064.
8. Bernhammer JC, Frison G, Huynh HV (2013) Electronic structure trends in N-heterocyclic carbenes (NHCs) with varying number of nitrogen atoms and NHC-transition-metal bond properties. Chemistry 19: 12892-12905.
9. Mendoza-Espinosa D, González-Olvera R, Negrón-Silva GE, Angeles-Beltrán D, Santillan R, et al. (2015) Phenoxy-linked mesoionic triazol-5-ylidenes as platforms for multinuclear transition metal complexes. Organometallics 34: 4529-4542.
10. Nguyen TV, Yoo WJ, Kobayashi S (2015) Effective Formylation of Amines with Carbon Dioxide and Diphenylsilane Catalyzed by Chelating bis(tzNHC) Rhodium Complexes. Angew Chem Int Ed Engl 54: 9209-9212.
11. Maity R, van der Meer M, Hohloch S, Sarkar B (2015) Di- and trinuclear iridium(III) complexes with poly-mesoionic carbenes synthesized through selective base-dependent metalation. Organometallics 34: 3090-3096.
12. Dasgupta A, Ramkumar V, Sankararaman S (2015) Catalytic asymmetric hydrogenation using a [2.2] paracyclophane based chiral 1,2,3-triazol-5-ylidene–Pd complex under ambient conditions and 1 atmosphere of H_2. RSC Adv 5: 21558-21561.
13. Mitsui T, Sugihara M, Tokoro Y, Fukuzawa S (2015) Synthesis of adamantyl substituted 1,2,3-triazol-5-ylidene ligands and their PEPPSI-type palladium complexes. Tetrahedron 71: 1509-1514.
14. Schuster EM, Botoshansky M, Gandelman M (2011) 1,2,3-Triazolylidene based complexes via post-modification of pincer click ligands. Dalton Trans 40: 8764-8767.
15. Schulze B, Escudero D, Friebe C, Siebert R, Görls H, et al. (2011) A heteroleptic bis(tridentate) ruthenium(II) complex of a click-derived abnormal carbene pincer ligand with potential for photosensitzer application. Chemistry 17: 5494-5498.
16. Bezuidenhout DI, Kleinhans G, Guisado-Barrios G, Liles DC, Ung G, et al. (2014) Isolation of a potassium bis(1,2,3-triazol-5-ylidene)carbazolide: a stabilizing pincer ligand for reactive late transition metal complexes. Chem Commun (Camb) 50: 2431-2433.
17. Liu Y, Kjaer KS, Fredin LA, Chábera P, Harlang T, et al. (2015) A heteroleptic ferrous complex with mesoionic bis(1,2,3-triazol-5-ylidene) ligands: taming the MLCT excited state of iron(II). Chemistry 21: 3628-3639.
18. Correa A, García Mancheño O, Bolm C (2008) Iron-catalysed carbon-heteroatom and heteroatom-heteroatom bond forming processes. Chem Soc Rev 37: 1108-1117.
19. Bolm C, Legros J, Le Paih J, Zani L (2004) Iron-catalyzed reactions in organic synthesis. Chem Rev 104: 6217-6254.
20. Majumdar KC, De N, Ghosh T, Roy B (2014) Iron-catalyzed synthesis of heterocycles. Tetrahedron 70: 4827-4868.
21. Bauer I, Knölker HJ (2015) Iron catalysis in organic synthesis. Chem Rev 115: 3170-3387.
22. Plietker (2011) Iron catalysis. Springer-Verlag, Berlin.
23. Iwasaki H, Koga Y, Ishikawa R, Yamada Y, Matsubara K (2015) Isolation and structures of 1,2,3-triazole-derived mesoionic biscarbenes with bulky aromatic groups. Eur J Org Chem. In Press.
24. Kochi JK (1980) The role of electron transfer and charge transfer in organometallic chemistry. Pure & Appl Chem 52: 571-605.
25. Holmes BT, Pennington WT, Hanks TW (2003) Efficient Synthesis of a Complete Donor/Acceptor bis(Aryl)diyne Family. Synthetic Commun 33: 2447-2461.
26. Pilyugina TS, Schrock RR, Hock AS, Müller P (2005) Synthesis of molybdenum(VI) monoimido alkyl and alkylidene complexes. Organometallics 24: 1929-1937.
27. Burla MC, Caliandro R, Camalli M, Carrozzini B, Spagna R, et al. (2007) SIR2008: Program for the solution of crystal structures from X-ray data. CNR Institute of Crystallography, Bari, Italy.
28. Gruene T, Hahn HW, Luebben AV, Meilleur F, Sheldrick GM (2013) Refinement of macromolecular structures against neutron data with SHELXL2013. J Appl Crystallogr 47: 462-466.
29. Danopoulos AA, Tsoureas N, Wright JA, Light ME (2004) N-Heterocyclic pincer dicarbene complexes of iron(II): C-2 and C-5 metalated carbenes on the same metal center. Organometallics 23: 166-168.