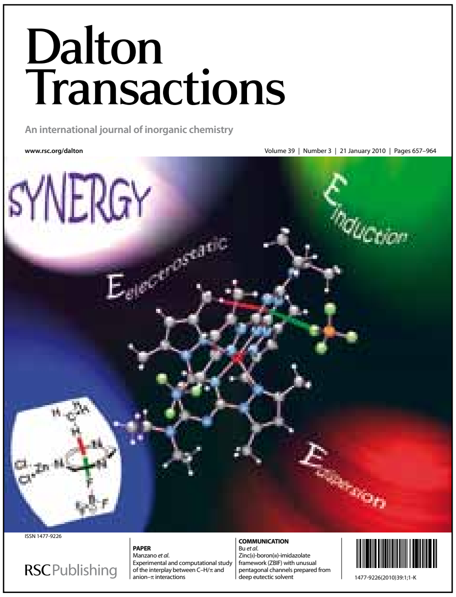
View Article Online / Journal Homepage

Dalton Transactions

Accepted Manuscript

Downloaded by FORDHAM UNIVERSITY on 01 December 2012
Published on 30 November 2012 on http://pubs.rsc.org | doi:10.1039/C2DT32368K



Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 39 | Number 3 | 21 January 2010 | Pages 657–964

ISSN 1477-9226

RSC Publishing

PAPER
Manzano *et al.*
Experimental and computational study of the interplay between C–H/π and anion–π interactions

COMMUNICATION
Bu *et al.*
Zinc(II)-boron(III)-imidazolate framework (ZBIF) with unusual pentagonal channels prepared from deep eutectic solvent

1477-9226(2010)39:1;1-K

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSC Publishing

www.rsc.org/dalton

Registered Charity Number 207890

Dynamic Article Links ►

View Article Online

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Position-Selective Intramolecular Aromatic C-H Bond Activation of 1,2,3-Triazol-5-ylidene (tzNHC) Ligands in (*p*-Cymene)Ruthenium(II) Complexes

Kenichi Ogata, Sayuri Inomata and Shin-ichi Fukuzawa*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A series of 1,2,3-triazol-5-ylidene (tzNHC) complexes of a (*p*-cymene)ruthenium system was synthesized. The reactivity of the *N*-bonded and *C*-bonded aryl groups in the tzNHC ligand was found to be significantly different with respect to intramolecular aromatic C-H bond activation.

N-Heterocyclic carbenes (NHCs) have emerged as an extremely useful class of ligands for use in transition metal complexes.[1] The majority of NHC ligands are imidazol-2-ylidenes **A** or 1,2,4-triazol-5-ylidenes **B** (Fig. 1), which are classified as normal NHCs. In contrast, since Crabtree first described an NHC complex in which the imidazolium moiety was coordinated at the C4 position (**C**),[2] alternative NHC ligands (mesoionic NHCs) have been reported.[3] In this category, following the first description of the 1,2,3-triazol-5-ylidene ligand (tzNHC, **D**) and its complex by Albrecht et al.,[4] several research groups have reported the synthesis of transition metal complexes bearing the tzNHC ligand, as well as their application to catalytic transformations.[5] Our research group has reported the synthesis of palladium and copper complexes bearing the tzNHC ligand and their application to catalytic organic reactions.[6] In these studies, the tzNHC complexes showed higher catalytic activity than the corresponding imidazole NHC system in organic reactions. It is known that the electron donating ability of the tzNHC ligand toward the metal fragment is higher than that of the normal imidazol-2-ylidene ligand,[4] and its electronic properties affect its catalytic activity in transition-metal-catalyzed organic reactions. Although the catalytic merit and electronic properties of the 1,2,3-triazol-5-ylidene ligand have been examined, an investigation of the character of the two environmentally different substituents (*N*- and *C*-bonded) of the NHC ligand, derived from its unsymmetrical ligand structure, has yet to be developed. To obtain information about this point, we turned our attention to an examination of the intramolecular aromatic C-H bond activation (*ortho* metalation) of a 1,2,3-triazol-5-ylidene ligand bearing two aryl substituents. The report for *ortho* metallation of tzNHC ligand has scarcely been studied.[7,8] In case of palladium complexes, it has been described that *N*-bonded aryl group of tzNHC ligand is prefer to undergo a *ortho* metalation.[8] However research about this point had yet to be studied in detail.

In this communication, we report the synthesis of a series of 1,2,3-triazol-5-ylidene complexes of a (*p*-cymene)ruthenium(II) system to compare the reactivity of *N*-bonded and *C*-bonded aryl groups in the tzNHC ligand toward *ortho* metalation at the metal centre. [9,10]

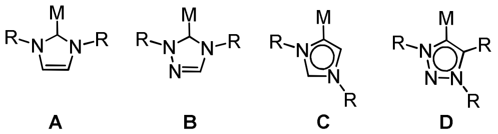
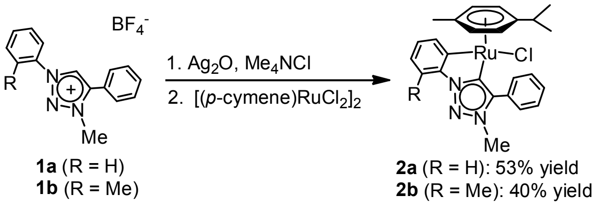


Fig. 1 Normal NHC (**A** and **B**) and mesoionic NHC ligands (**C** and **D**)

To prepare the ruthenium complexes bearing the 1,2,3-triazol-5-ylidene ligands, transmetalation from the corresponding *in situ* generated silver carbene complexes was effected using Ag_2O and tetramethylammonium chloride.[11] Treatment of phenyl-substituted triazolium salt **1a** with 0.6 equiv of silver oxide and tetramethylammonium chloride, followed by reaction with 0.5 equiv of $[(p\text{-cymene})RuCl_2]_2$, led to the formation of (*p*-cymene)RuCl(tzNHC) complex **2a**, in which the *N*-bonded phenyl group of the tzNHC ligand was metalated at the *ortho* position by ruthenium (Scheme 1).[12] This complex was obtained as a single product; the ruthenium complex that would result from metalation of the *C*-bonded phenyl ring was not formed.[13] In the case of the reaction in THF under reflux conditions, formation of complex **2a** was also confirmed by ^1H NMR, and the complex **2a** was not converted to *C*-bonded phenyl metalated product. This result indicated that ruthenium metal activation of the aromatic C-H bond in the *N*-bonded phenyl ring occurred more easily than that of the *C*-bonded phenyl ring. In the reaction using triazolium salt **1b** bearing an *o*-tolyl group at the 1-position instead of a phenyl group, selective formation of the corresponding ruthenium complex **2b** also proceeded, with C-H bond activation of the *o*-tolyl group. These complexes were characterized by ^1H and ^{13}C NMR analysis. By ^1H NMR, the two isopropyl methyl groups of the *p*-cymene ligand were observed as two doublet signals at 0.73 and 0.82 ppm for **1a** and 0.73 and 0.80 ppm for **1b**, indicating unsymmetrical molecular structures. The ^{13}C NMR spectra showed characteristic signals for the carbene carbons at 166.3 (**1a**) and 167.6 ppm (**1b**),[14] and the ruthenium-bonded phenyl carbons were observed at 173.0 (**1a**) and 174.2 ppm (**1b**).

The structures of complexes **2a** and **2b** were also confirmed by X-ray analysis (Fig. 2), which revealed the existence of covalent bonds between the ruthenium metal and the *N*-bonded aryl substituents of the tzNHC ligands at the *ortho* position. The Ru-

C(carbene) bond distances of **2a** and **2b** were 2.037(3) and 2.025(4) Å, respectively. These bond distances were within the normal range for previously reported 1,2,3-triazol-5-ylidene ruthenium(II) complexes.[4] The Ru-C(η^1-aryl) bond distances in **2a** (2.080(2) Å) and **2b** (2.068(4) Å) were similar in value to the corresponding imidazol-2-ylidene (*p*-cymene) ruthenium complex involving an *ortho*-metalated phenyl group in the ligand.[10]



Scheme 1 Synthesis of ruthenium complexes involving C-H bond activation of the *N*-bonded aryl group in the tzNHC ligand.

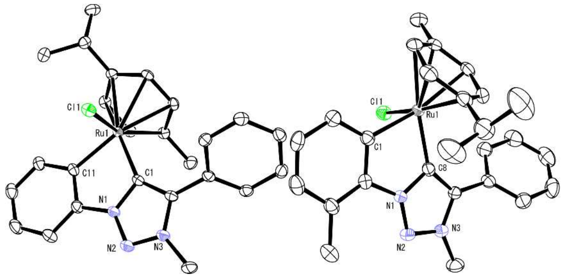
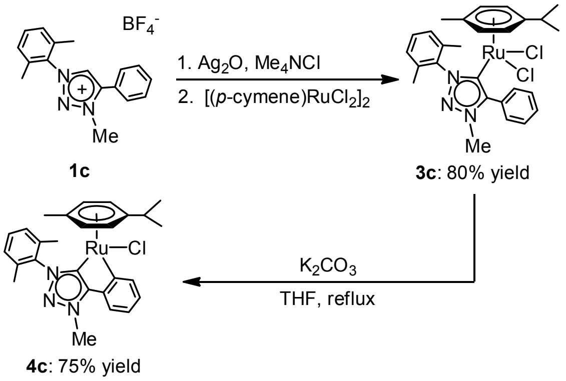


Fig. 2 ORTEP drawings of **2a** (left) and **2b** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and solvents are omitted for clarity.

We next investigated the reaction of 1-(2,6-xylyl)-4-phenyl-triazol-5-ylidene for which aromatic intramolecular C-H bond activation of the aryl moiety at the *ortho* position by the ruthenium complex was not possible (Scheme 2). The reaction of *in situ* generated silver tzNHC, derived from the corresponding triazolium salt **1c**, with [(*p*-cymene)RuCl$_2$]$_2$ resulted in the formation of tzNHC ruthenium complex **3c** in 80% yield. In spite of the presence of aromatic C-H bonds at the *ortho* positions of the *C*-bonded phenyl group of this tzNHC ligand, metalation of these positions did not occur under the same reaction conditions that produced complex **2** in Scheme 1. This noteworthy result indicated that the reactivity of the *N*-bonded and *C*-bonded aryl groups of the tzNHC ligands was considerably different, and the *C*-bonded aryl group was less likely to undergo metalation than the imidazole NHC ligand.[9] To abstract the hydrogen atom from the phenyl ring and the chloride ligand from complex **3c** and synthesize the tzNHC complex *ortho*-metalated at the *C*-bonded phenyl ring, the reaction of **3c** with base was carried out (Scheme 2). Upon treatment of **3c** with K_2CO_3 in THF under reflux conditions for 6 h, *ortho*-metalated complex **4c** was obtained in 75% yield. ^{1}H NMR signals for the isopropyl methyl protons of **4c** were observed as two doublets at 0.51 and 0.92 ppm, whereas those of **3c** were observed as one doublet at 1.16 ppm. The carbene carbon of **3c** was observed at 162.4 ppm by ^{13}C NMR. In contrast, ^{13}C NMR measurement of **4c** showed two characteristic low field signals at 178.4 and 180.8 ppm. The structures of **3c** and **4c** were also confirmed by X-ray analysis (Fig. 3). The Ru-C(carbene) bond distance in **4c** (2.0225(19) Å) was similar in value to **2a** and **2b**, whereas the Ru-C(carbene) bond distance in **3c** (2.102(6) Å) was longer than in the complexes involving *ortho*-metalated structures (**2a**, **2b**, and **4c**). In the case of **4c**, the bond distance for Ru-C(η^1-phenyl) (2.0860(17) Å) was almost the same as that in complex **2**.

As described above, when the reaction site in the *N*-bonded aryl group of the tzNHC ligand was protected, *ortho* metalation of the *C*-bonded phenyl group could be controlled. The difference between the *ortho*-metalation reactivity in the *N*- and *C*-bonded aryl groups probably derived from two factors: (i) *N*-bonded aryl substituents are probably more electron-rich than *C*-bonded ones and its affect the position selective *ortho* metalation. (ii) For steric reasons, the *C*-bonded phenyl ring would appear to be oriented perpendicular to the triazole ring due to the steric repulsions with methyl group at the 3-position. This precludes the *C*-bonded phenyl ring from approaching the ruthenium metal with the orientation needed for C-H bond activation to occur.



Scheme 2 Synthesis of ruthenium complex bearing 1-(2,6-xylyl)-4-phenyl-triazol-5-ylidene **3c**, and reaction of **3c** with K_2CO_3.

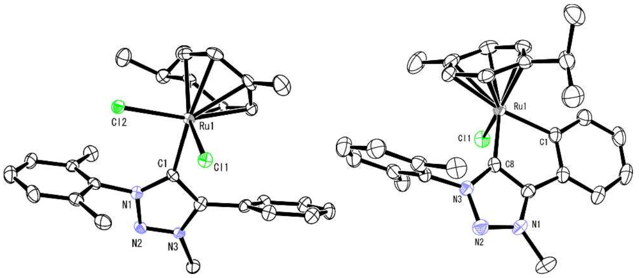
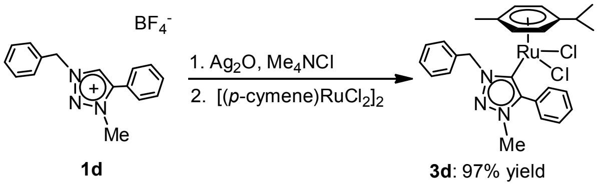


Fig. 3 ORTEP drawings of **3c** (left) and **4c** (right) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and solvents are omitted for clarity.

Replacement of the 2,6-xylyl group with a benzyl group in the tzNHC ligand resulted in the formation of the corresponding ruthenium complex **3d** in 97% yield, which was not *ortho*-metalated at the *C*-bonded phenyl group (Scheme 3). [15]



View Article Online

Scheme 3 Synthesis of ruthenium complex bearing 1-benzyl-4-phenyl-triazol-5-ylidene **3d**.

In summary, the preparation of ruthenium(II) complexes bearing 1,2,3-triazol-5-ylidene ligands was achieved. This system was used to demonstrate the unique properties of the 1,2,3-triazol-5-ylidene ligands derived from their unsymmetrical structures. It was confirmed that the reactivity of the *N*-bonded and *C*-bonded aryl groups of the tzNHC ligand toward intramolecular aromatic C-H bond activation (*ortho* metalation) was significantly different. These results offer important and useful information about the coordination chemistry of triazole NHC complexes and their use as catalysts. Further investigation in this area is currently ongoing in our laboratory.

This work was financially supported by a Chuo University Grant for Special Research. We are grateful to Prof. Yoshiaki Nishibayashi and Dr. Yoshiaki Tanabe (University of Tokyo) for their help with X-ray measurements.

Notes and references

Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan. Fax: +81-3-3817-1895; Tel: +81-3-3817-1916; E-mail: orgsynth@kc.chuo-u.ac.jp

† Electronic Supplementary Information (ESI) available:full experimantal procedure and data. See DOI: 10.1039/b000000x/

‡ CCDC 901766 (**2a**), 901767 (**2b**), 901768 (**3c**) and 901934 (**4c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1 For reviews of *N*-heterocyclic carbenes, see: W. A. Herrmann, *Angew. Chem. Int. Ed*. 2002, **41**, 1290; N. Marion and S. P. Nolan, *Chem. Soc. Rev*., 2008, **37**, 1776; S. Würtz and F. Glorius, *Acc. Chem. Res.* 2008, **41**, 1523; K. Cavell, *Dalton Trans.* 2008, 6676; F. E. Hahn and M. C. Jahke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122.

2 S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.* 2001, 2274.

3 P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596; M. Albrecht, *Chem. Commun.*, 2008, 3601; O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.* 2009, **109**, 3445.

4 P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534.

5 For example: K. J. Kilpin, U. S. D. Paul, A.-L. Lee, J. D. Crowley, *Chem. Commun.*, 2011, 328; A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels and M. Albrecht, *Organometallics*, 2011, **30**, 1021; J. Bouffard, B. K. Keitz, R. Tonner, G. Guisado-Barrios, G. Frenking, R. H. Grubbs and G. Bertland, *Organometallics*, 2011, **30**, 2617; J. D. Crowley, A.-L. Lee, K. J. Kilpin, *Aust, J. Chem.*, 2011, **64**, 1118; K. J. Kilpin, U. S. D. Paul, A.-L Lee and J. D. Crowley, *Chem. Commun.*, 2011, **47**, 328; D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak and M. Albrecht, *Chem. Eur. J.* 2012, **18**, 6055.

6 T. Nakamura, K. Ogata and S.-i. Fukuzawa, *Chem. Lett.*, 2010, **39**, 920; T. Nakamura, T. Terashima, K. Ogata and S.-i. Fukuzawa, *Org. Lett.,* 2011, **13**, 620; S. Inomata, H. Hiroki, T. Terashima, K. Ogata and S.-i. Fukuzawa, *Tetrahedron Lett.*, 2011, **67**, 7263; T. Terashima, S. Inomata, K. Ogata and S.-i. Fukuzawa, *Eur. J. Inorg. Chem*., 2012, 1387; H. Inomata, K. Ogata, S.-i. Fukuzawa and Z. Hou, *Org. Lett.*, 2012, **14**, 3986.

7 R. Lalrempuia, N. D. McDaniel, H. Müller-Bunz, S. Bernhard and M. Albrecht, *Angew. Chem. Int. Ed.*, 2010, **49**, 9765; A. Petronilho, M. Rahman, J. A. Woods, H. Al-Sayyed, H. Müller-Bunz, J. M. Don MacElroy, S. Bernhard and M. Albrecht, Dalton Trans., 2012, **41**, 13074; K. Donnelly, M. Albrecht, XXV International Conference on Organometalic Chemistry, Lisbon, 2012, abstract F.2.23.

8 R. Saravankumar, V. Ramkumar and S. Sankararaman, *Organometallics*, 2011, **30**, 1689.

9 Report for intramolecular aromatic C-H bond activation of imidazole NHC ligand on ruthenium(II) complex, for example: P. B. Hitchcock, M. F. Lappert, P. L. Pye and S. Thomas, *J. Chem. Soc., Dalton Trans.*, 1979, 1929.

10 Intramolecular aromatic C-H bond activation of imidazole NHC ligand on (*p*-cymene)ruthenium system has been repoted: C. Zhang, Y. Zhao, B. Li, H. Song, S. Xu and B. Wang, *Dalton Trans.*, 2009, 5182.

11 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972; J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978.

12 The (η^6-arene)ruthenium complexes bearing 1,2,3-triazol-5-ylidene which not involve aromatic C-H bond activation of ligand have been reported by Albrecht *et al.*: A. Prades, E. Peris and M. Albrecht, *Organometallics*, 2011, **30**, 1162; L. Bernet, R. Lalrempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet and M. Albrecht, *Chem. Commun.,* 2011, **47**, 8058. and ref.4.

13 In the case of NMR tube reaction between [(p-cycmene)RuCl$_2$]$_2$ and silver salt of **1a** in CD$_2$Cl$_2$ at room temperatre for 3 h, product **2a** was detected as single NHC complex product by ^{1}H NMR measurement, and unreacted starting complex [(p-cycmene)RuCl$_2$] was also confirmed. Other ruthenium complex was not detected.

14 These values are the normal range of previously reported (*p*-cymene)ruthenium complex bearing 1,2,3-triazole-5-ylidene. See ref. 9

15 Although the reaction of **3d** with K$_2$CO$_3$ was carried out under THF reflux, *ortho*-metalated complex was not formed and **3d** was recovered.

(*p*-cymene)ruthenium complex bearing 1,2,3-triazol-5-ylidene (tzNHC) ligand involving position selective intramolecular aromatic C-H bond activation were synthesized. As a result, it was found that the reactivity between *N*-bonded and *C*-bonded aryl group in tzNHC ligand for the C-H bond activation is significantly different.