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Abnormal oxazol-4-ylidene and thiazol-4-ylidene rhodium complexes: synthesis, structure, and properties†

Jun Zhang,*[a] Jun Fu,[a] Xiaolong Su,[a] Xinke Qin,[a] Meixin Zhao[a] and Min Shi*[ab]

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A series of new 2,3,5-triaryl-substituted oxazolium and thiazolium salts are readily prepared by a Tf_2O-mediated intramolecular cyclisation and their use as precursors for the synthesis of novel oxazol-4-ylidene and thiazol-4-ylidene rhodium complexes has been developed.

Over the last decade, *N*-heterocyclic carbenes (NHCs) have received much attention mainly due to their widespread and spectacular applications as organocatalysts and as ligands for organometallic catalysis.[1] The vast majority of NHCs are based on 5-membered ring systems, among which the most important and most often employed NHCs are imidazol-2-ylidenes **A** (Fig. 1). In the complexes supported by NHC of type **A**, the metals are generally bonded in the 2-position of the imidazole ring. Crabtree *et al*. first reported an "abnormal" NHC (*a*NHC) complex featuring an imidazol-5-ylidene **B** as a ligand,[2a] in which the imidazole moiety is coordinated at the C5 position. From then on, besides **B**-type *a*NHC,[2] other types of *a*NHCs were also reported, such as pyrazolin-4-ylidenes **C**[3] and 1,2,3-triazol-5-ylidenes **D**.[4] Very recently, Bertrand *et al*. reported a series of transition metal complexes based on thiazol-5-ylidenes (**E**), in which the *a*NHCs have only one exocyclic substituent adjacent to the carbenic center.[5] Bertrand *et al*. found that ethynyl dithiocarbamate **F** can act as a ligand equivalent of cyclic mesoionic carbene 1,3-dithiol-5-ylidene **G**.[6] During the course of this work, we became aware of the very recent independent publication by Bertrand *et al*. of ynamide **H** acting as a ligand equivalent of oxazol-4-ylidene **I**.[7] Experimental and theoretical data showed that the *a*NHCs are more basic than their normal NHC congeners, affording unique and spectacular performance in catalysis.[8,9]

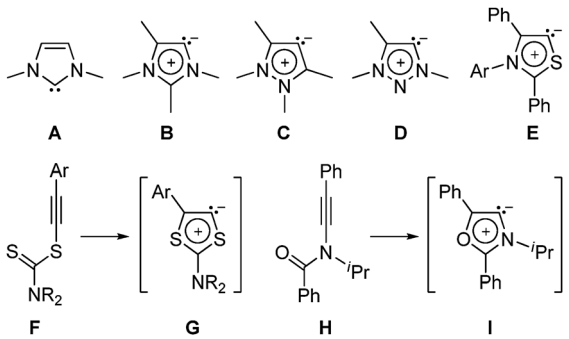


Fig. 1 Imidazol-2-ylidene (**A**), selected examples of five-membered *a*NHC (**B–E**, **G**, **I**), dithiocarbamate **F**, and ynamide **H**.

In 2009, Bertrand *et al*. first isolated a crystalline metal-free *a*NHC imidazol-5-ylidene **J** (Fig. 2).[2f] To offer kinetic protection to the C5 position, they appended bulky 2,6-diisopropylphenyl (Dipp) substituents at both nitrogen atoms and a phenyl group at C4. Later on, Bertrand *et al*. also reported the isolation of crystalline free *a*NHCs 1*H*-1,2,3-triazol-5-ylidenes (**K**) having two neighboring aryl substituents.[4e] The protection offered by the two exocyclic aryl substituents adjacent to the carbenic center practically stabilizes the free *a*NHC, and thus makes **J** exhibit excellent performance not only as an organocatalyst in ring opening polymerization of cyclic esters[10a] but also as a ligand in Pd-catalyzed Suzuki–Miyaura cross coupling of aryl chlorides at room temperature.[10b] Very recently, we have established a Tf_2O-mediated intramolecular cyclization reaction for the facile synthesis of a series of backbone-substituted saturated imidazolinium salts,[11a,b] and various unsaturated NHC precursors, such as imidazolium, imidazopyridinium, and oxazolium salts, and prepared a Rh complex based on NHC **L** derived from the oxazolium salt,[11c] the first example of oxazolin-2-ylidene with a steric demanding aryl *N*-substituent. These findings inspired us to synthesize *a*NHC oxazol-4-ylidene **M** and its congener thiazol-4-ylidene **N**, placing two exocyclic aryl substituents

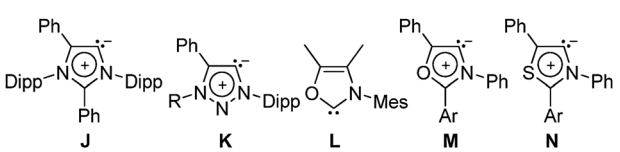
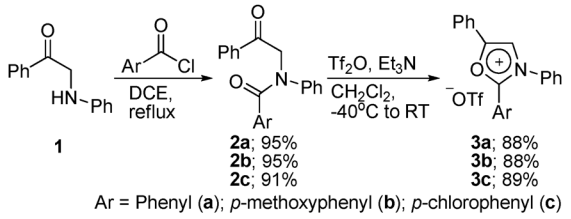


Fig. 2 Isolable crystalline *a*NHC (**J** and **K**), related oxazolin-2-ylidene (**L**), and the targeted oxazol-4-ylidene (**M**) and thiazol-4-ylidene (**N**).

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237, China. E-mail: zhangj@ecust.edu.cn; Tel: +86 021 64252995*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China. E-mail: mshi@mail.sioc.ac.cn; Tel: +86 021 64252995*

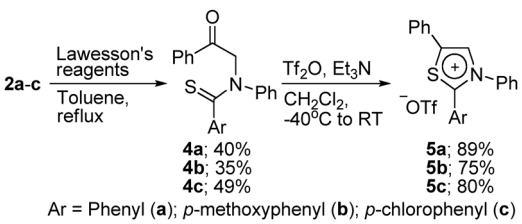
† Electronic supplementary information (ESI) available: Experimental and spectroscopic data for all compounds. CCDC 887373 (**5a**), 887374 (**5b**), 885472 (**6a**), and 885473 (**7a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc35020c



Scheme 1 Synthesis of oxazolium salts **3a–c**.

adjacent to their carbenic center. Herein we report the preparation of a series of new oxazolium and thiazolium salts, and their use for the preparation of Rh complexes based on the novel *a*NHCs **M** and **N**.

Formamide derivatives **2a–c** were prepared by the reaction of three benzoyl chlorides and **1** in 91–95% yields, respectively, by a literature method[12] (Scheme 1). Using a Tf_2O-mediated intramolecular cyclization, in the presence of Tf_2O/Et_3N, **2a–c** underwent cyclization to afford the desired 2,3,5-triaryl-substituted oxazolium salts **3a–c** in 88–89% yields. Both mass and the characteristic signal between 8.14 and 9.14 ppm (oxazolium C–H) in the ^{1}H NMR spectra confirmed the formation of the oxazolium salts. Encouraged by the results, we further attempted to synthesize the congeners of **3a–c**, thiazolium salts. **2a–c** were treated with the Lawesson's reagents to afford **4a–c** in 35–49% yields, which underwent cyclization to produce the corresponding 2,3,5-triaryl-substituted thiazolium salts **5a–c** in 75–89% yields in the presence of Tf_2O/Et_3N (Scheme 2). Both mass and the characteristic signal between 8.23 and 8.39 ppm (thiazolium C–H) in the ^{1}H NMR spectra, and in particular the X-ray diffraction analysis of **5a** and **5b** (Fig. 3) confirmed the formation of the thiazolium salts **5a–c**.



Scheme 2 Synthesis of thiazolium salts **5a–c**.

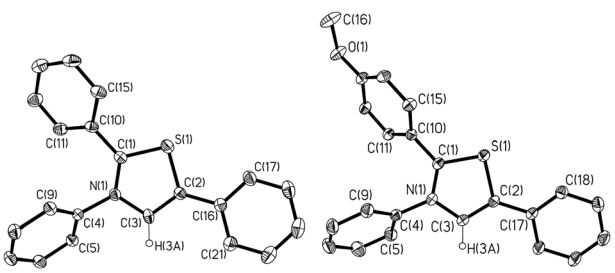
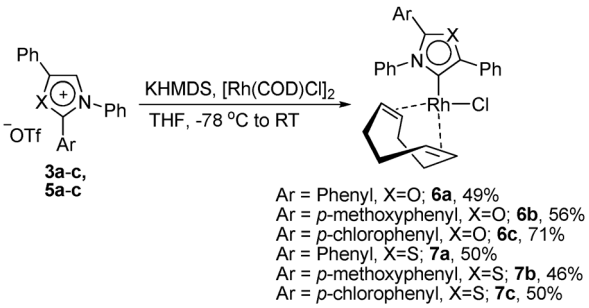


Fig. 3 Molecular structure of thiazolium salts **5a** (left) and **5b** (right) with 30% probability. H atoms and the anion (OTf^-) have been omitted for clarity. Selected bond distances (Å) and angles (°): **5a**: N(1)–C(3) 1.411(3), S(1)–C(1) 1.681(3), S(1)–C(2) 1.720(3), C(2)–C(3) 1.379(3), C(1)–S(1)–C(2) 91.97(12), C(2)–C(3)–N(1) 110.1(2), C(3)–C(2)–S(1) 111.3(2); **5b**: S(1)–C(1) 1.679(4), S(1)–C(2) 1.724(4), N(1)–C(3) 1.370(4), C(2)–C(3) 1.337(5), C(1)–S(1)–C(2) 91.69(17), C(1)–N(1)–C(3) 113.6(3), N(1)–C(1)–S(1) 111.2(2), C(3)–C(2)–S(1) 109.8(2), C(2)–C(3)–N(1) 113.6(3).



Scheme 3 Synthesis of Rh complexes **6a–c** and **7a–c**.

Bertrand *et al*. previously reported that the deprotonation of the *N*-^{i}Pr-3,5-diphenylsubstituted oxazolium triflate salt, an analogue of **3a**, yielded the ynamide **H** (Fig. 1), while, under the same conditions, the deprotonation of **3a** by $KN(SiMe_3)_2$ (KHMDS) in Et_2O only resulted in complex mixtures, probably due to high sensitivity of the desired free oxazol-4-ylidene. Then the deprotonation of the corresponding formamidinium salts **3a–c** or **5a–c** by KHMDS in the presence of $[(COD)RhCl]_2$ led to the formation of the expected oxazol-4-ylidene-based Rh complexes **6a–c** and thiazol-4-ylidene-based Rh complexes **7a–c** in 46–71% yields (Scheme 3). Complexes **6a–c** and **7a–c** are robust, thermally stable solids, and could be chromatographically purified on silica-gel. NMR and ESI analyses, and in particular the X-ray diffraction analysis of **6a** and **7a** (Fig. 4) confirmed the formation of these *a*NHC-based Rh complexes. The C(carbene)–Rh bond distance of 2.034(3) Å for **6a** is shorter than that of 2.052(4) Å for **7a** and that reported for [RhCl(*a*NHC)(cod)] (*a*NHC = 2-mesityl-3-phenylimidazo-[1,5-*a*]pyridine-1-ylidene, 2.043 Å),[2d] and is longer than those reported for [RhCl(NHC)(cod)] (NHC = oxazol-2-ylidene **H**, 2.017(4) Å;[11c] NHC = 1,3-dimethylimidiazolin-2-ylidene, 2.023(2) Å)[13] and that reported for [RhCl(*a*NHC)(cod)] (*a*NHC = 1,3-disubstituted-1,2,3-triazolylidene, 2.027(6) Å).[4a]

To evaluate the electron-donating ability of these new *a*NHCs, **6a–c** and **7a–c** were treated with excess carbon monoxide,

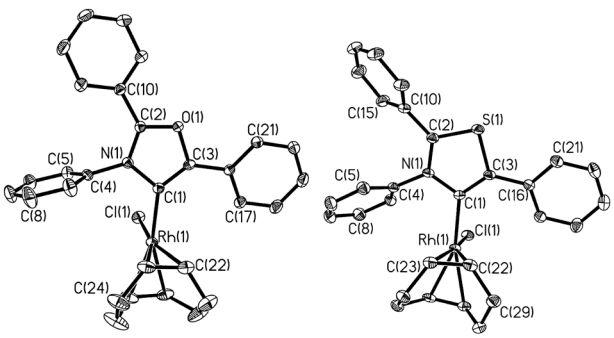
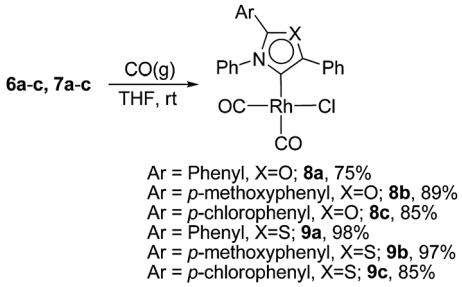


Fig. 4 Molecular structure of **6a** (left) and **7a** (right) with 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): **6a**: Rh(1)–C(1) 2.034(3), Rh(1)–Cl(1) 2.3792(16), O(1)–C(2) 1.317(3), O(1)–C(3) 1.408(3), N(1)–C(1) 1.425(3), C(1)–C(3) 1.360(4), C(2)–O(1)–C(3) 107.2(2), C(3)–C(1)–N(1) 102.6(2), O(1)–C(2)–N(1) 109.3(2), C(1)–C(3)–O(1) 110.0(2); **7a**: Rh(1)–C(1) 2.052(4), Rh(1)–Cl(1) 2.418(2), S(1)–C(2) 1.690(4), S(1)–C(3) 1.750(4), N(1)–C(1) 1.415(5), C(1)–C(3) 1.374(5), C(2)–S(1)–C(3) 91.89(18), C(2)–N(1)–C(1) 117.0(3), C(3)–C(1)–N(1) 108.9(3), C(1)–C(3)–S(1) 111.8(3).



Scheme 4 Synthesis of dicarbonyl Rh complexes **8a–c** and **9a–c**.

which afforded the Rh dicarbonyl species **8a–c** and **9a–c** in 75–98% yields, respectively. Although there is some limitation of the method for evaluating ligand donor properties,[4j,14] the average CO vibration frequency of the Rh carbonyl complexes **8a–c** (ν_{av} = 2026–2028 cm^{-1}) and **9a–c** (ν_{av} = 2021–2022 cm^{-1}) suggests that the corresponding thiazol-4-ylidenes are probably stronger than the corresponding oxazol-4-ylidenes (Scheme 4).

In conclusion, we have established a facile and modular method for the preparation of a series of new 2,3,5-triaryl-substituted oxazolium and thiazolium salts. The oxazolium and thiazolium salts can act as precursors for the synthesis of novel oxazol-4-ylidene and thiazol-4-ylidene rhodium complexes, which are robust and thermally stable. Future work will be aimed at investigating the applications of these novel *a*NHC ligands in transition-metal catalyzed reaction.

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