Cite this: Chem. Commun., 2011, 47, 10614-10616

## COMMUNICATION

## Mesoionic thiazol-5-ylidenes as ligands for transition metal complexes<sup>†</sup>

Daniel Mendoza-Espinosa, Gaël Ung, Bruno Donnadieu and Guy Bertrand\*

*Received 11th July 2011, Accepted 27th July 2011* DOI: 10.1039/c1cc14165a

The first examples of thiazol-5-ylidene complexes featuring group 9, 10 and 11 metal centers, have been prepared by deprotonation of a series of 2,3,4-triaryl-substituted thiazolium salts in the presence of the corresponding transition metal precursor.

In 2001, Crabtree et al. reported the preparation of complex **B**,<sup>1</sup> featuring an imidazol-5-ylidene **C** as ligand. It was quickly demonstrated that these types of ligands<sup>2</sup> are even stronger electron-donors than their imidazol-2-ylidene isomers, the so-called NHCs A<sup>3,4</sup> (Fig. 1). Recently, it has been shown that derivatives of type C<sup>5</sup>, as well as pyrazolin-4-ylidenes  $D^6$  and 1,2,3-triazol-5-ylidenes  $\mathbf{E}$ ,<sup>7</sup> can be isolated. Since no reasonable canonical resonance forms showing a carbene can be drawn without additional charges, and since they are mesoionic compounds, they can be named mesoionic carbenes (MICs).<sup>8</sup> Importantly, in contrast to regular carbenes, no obvious dimerization pathway can be foreseen, and therefore it was reasonable to believe that unhindered MICs with various heteroatom-containing skeletons could be stable. To test this hypothesis, we attempted the preparation of 1,3-dithiol-5ylidenes F, but observed a spontaneous ring opening yielding the corresponding ethynyl dithiocarbamate G.9 The formation of **G** is reminiscent of the ring-opening reaction observed in the deprotonation of isothiazolium salts,<sup>10</sup> and therefore is probably due to the weakness of the sulfur-carbon bond. These results prompted us to investigate the preparation of thiazol-5-ylidenes H, since a similar ring-opening process would imply the cleavage of a carbon-nitrogen bond. Moreover, although 1,3-dithiol-2-ylidenes I have never been observed, it is noteworthy that 1,3-thiazol-2-ylidenes J have been used for decades as organocatalysts,<sup>11</sup> beginning with the seminal work by Breslow,<sup>12</sup> before their isolation by Arduengo.<sup>13</sup> Here we report the synthesis of a series of 2,3,4-aryl-substituted thiazolium salts, and their use for the preparation of thiazol-5-ylidene transition metal complexes.

2,3,4-Triaryl-substituted thiazolium salts **3a–c** are conveniently prepared in two steps from thioamides **1a–c** (Scheme 1). Addition of triethylamine in the presence of bromoacetophenone affords ketones **2a–c** in 55 to 76% yield. Then, cyclization under acidic conditions produces the desired thiazolium salts **3a–c** in 42 to 60% yields. In order to increase their solubility, a salt metathesis reaction with silver trifluoromethanesulfonate was carried out, producing **4a–c** in excellent yields. The formation of the thiazolium salts was confirmed by the characteristic downfield signal between 8.64 and 9.20 ppm (thiazolium C–H) in the <sup>1</sup>H NMR spectra and, in the case of salt **3b**, by a single crystal X-ray diffraction study (Fig. 2, left).‡

All attempts to deprotonate salts **3** and **4** with a variety of bases [MHMDS (M = Li, Na, K), "BuLi, KO'Bu and LDA] resulted in complex mixtures. Even monitoring the deprotonation reaction by NMR spectroscopy, at -50 °C, did not allow for the observation of the desired thiazol-5-ylidenes of type **H**. However, when salts **4a–c** were treated at -78 °C with an equimolar amount of LiHMDS, in the presence of (THT)AuCl or [Pd(Allyl)Cl]<sub>2</sub>, the corresponding thiazol-5-ylidene transition metal complexes were obtained and isolated in moderate to good yields (51 to 90%) (Scheme 2). The <sup>13</sup>C NMR chemical shifts of the carbene carbon of Au<sup>I</sup> (149.5 to 151.4 ppm) and Pd<sup>II</sup> (156.0 to 159.5 ppm) complexes are in the range observed for previously reported metal complexes featuring MICs **C–F**, <sup>5,9,14</sup> and as expected, at much higher field than those of classical NHCs.<sup>15</sup>

To unambiguously confirm the existence of the new thiazol-5-ylidene ligands, single crystals of complex **5b**, obtained by slow diffusion of hexane into a concentrated chloroform



Fig. 1 NHCs (A), Crabtree's imidazol-5-ylidene complex (B), types of MIC that have previously been isolated (C–E), transient 1,3-dithiol-5-ylidene (F) and its ring opened isomer (G), the targeted thiazol-5-ylidenes (H), the never-observed 1,3-dithiol-2-ylidenes I, and the isolated 1,3-thiazol-2-ylidenes J.

UCR-CNRS Joint Reserach Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California, Riverside CA 92521-0403, USA. E-mail: guy.bertrand@ucr.edu; Fax: (+1) 202 354 5267

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Preparation and spectroscopic data for all compounds, selected X-ray data for compounds **3b** and **5b**. CCDC 833533 and 833534. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14165a



Scheme 1 Synthesis of thiazolium salts 3a-c and 4a-c [Ar = Phenyl (a); 2,4,6-trimethylphenyl (b); 2,6-diisopropylphenyl (c)].



**Fig. 2** Crystal structures of thiazolium salt **3b** (left) and gold complex **5b** (right) with ellipsoids shown at 50% probability. Hydrogen atoms, except for the CH of **3b**, are omitted for clarity. Selected bond distances [Å] and angles [°]: **3b**: C(1)-S(1) = 1.716(6), C(1)-C(3) = 1.363(6), C(3)-N(1) = 1.397(3), N(1)-C(2) = 1.361(3), C(2)-S(1) = 1.684(2), C(3)-C(1)-S(1) = 112.0(4); **5b**: C(1)-S(1) = 1.697(14), C(1)-C(3) = 1.364(16), C(3)-N(1) = 1.414(15), N(1)-C(2) = 1.351(15), C(2)-S(1) = 1.695(14), Au(1)-C(1) = 2.005(14), Au(1)-Cl(1) = 2.293(4), C(3)-C(1)-S(1) = 110.0(10).



Scheme 2 Synthesis of metal complexes 5a-c and 6a-c [Ar = Phenyl (a); 2,4,6-trimethylphenyl (b); 2,6-diisopropylphenyl (c)].

solution, were subjected to an X-ray diffraction analysis (Fig. 2, right). Complex **5b** crystallizes in the C2/c space group displaying a monomeric unit with a Au(1)–C(1) bond distance of 2.005(14)Å, which is slightly longer that those observed for the (1,3-dithiol-5-ylidene)AuCl [1.978(4)Å]<sup>9</sup> and (imidazol-5-ylidene)AuCl [1.98 Å].<sup>5</sup> The carbene bond angle angle in **5b** [110.0(10)°] is slightly more acute than the corresponding angle of thiazolium salt **3b** [112.0(4)°]. This feature is consistent with the increased s-character of the  $\sigma$  lone-pair orbital on the carbene atom in **5b** as compared with the C–H<sup>+</sup> bond orbital in **3b**. Finally, as expected, the Au(1) center is in a linear environment with an C(1)–Au(1)–Cl(1) angle of 179.2(4)°.

To evaluate the donor properties of thiazol-5-ylidene ligands, the corresponding rhodium(1) dicarbonyl chloride complexes 7a-c were prepared by the *in situ* deprotonation



Scheme 3 Synthesis of the rhodium(1) complexes  $7\mathbf{a}-\mathbf{c}$  [Ar = Phenyl (a); 2,4,6-trimethylphenyl (b); 2,6-diisopropylphenyl = Dipp (c)].

of salts **4a–c**, at -78 °C, with LiHMDS, in the presence of half an equivalent of [Rh(COD)Cl]<sub>2</sub>, followed by treatment with an excess of carbon monoxide (Scheme 3).

The average CO vibration frequency for **7a–c** ( $\nu_{a\nu} = 2034$  cm<sup>-1</sup>) indicates that the electron-donor capabilities of thiazol-5-ylidenes are slightly superior to those of conventional NHCs ( $\nu_{a\nu} = 2039-2041$ cm<sup>-1</sup>),<sup>16</sup> similar to those of 1,3-dithiol-5ylidene **F** ( $\nu_{a\nu} = 2030$  cm<sup>-1</sup>)<sup>9</sup> and cyclic (alkyl)(amino)carbenes ( $\nu_{a\nu} = 2036$  cm<sup>-1</sup>),<sup>17</sup> but inferior to those of MICs **C–E** ( $v_{a\nu} = 2016-2025$  cm<sup>-1</sup>).<sup>2d</sup>

Although thiazol-5-ylidenes cannot be observed, the readily available 2,3,4-triaryl-substituted thiazolium salts are modular precursors for the synthesis of a variety of thiazol-5-ylidenes transition metal complexes. This novel type of MIC ligand features stronger donor properties than classical NHCs, and gives rise to complexes, which are thermally- and air-stable. Research in our laboratory is currently underway to extend the scope of mesoionic carbenes, and explore the catalytic activity of the corresponding complexes.

This work was supported by the NIH (R01 GM 68825) and DOE (DE-FG02-09ER16069).

## Notes and references

‡ Crystal data: **3b**: C<sub>27</sub>H<sub>30</sub>BrNO<sub>2</sub>S, M = 512.49, monoclinic, a = 9.4960(14), b = 28.054(4), c = 9.6399(14),  $\alpha = 90$ ,  $\beta = 104.693(2)$ ,  $\gamma = 90$ , V = 2484.1(6) Å<sup>3</sup>, T = 100(2) K, space group P2<sub>1</sub>/c, Z = 4, 20859 reflections measured, 6277 unique ( $R_{int} = 0.0276$ ), which were used in all calculations. The final R [I > 2sigma(I)] was 0.0319. **5b**: C<sub>24</sub>H<sub>21</sub>AuClNS, M = 587.89, monoclinic, a = 18.170(4), b = 9.7695(15), c = 24.734(4),  $\alpha = 90$ ,  $\beta = 99.134(3)$ ,  $\gamma = 90$ , V = 4334.9(12) Å<sup>3</sup>, T = 200(2) K, space group C2/c, Z = 8, 11994 reflections measured, 4607 unique ( $R_{int} = 0.0501$ ), which were used in all calculations. The final R [I > 2sigma(I] was 0.0648.

- S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274.
- For reviews on imidazol-5-ylidenes and related species, see:
   (a) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, Chem. Rev., 2009, 109, 3445;
   (b) M. Albrecht, Chem. Commun., 2008, 3601;
   (c) P. L. Arnold and S. Pearson, Coord. Chem. Rev., 2007, 251, 596;
   (d) M. Albrecht, Chimia, 2009, 63, 105;
   (e) M. Melaimi, M. Soleilhavoup and G. Bertrand, Angew. Chem., Int. Ed., 2010, 49, 8810.
- 3 For recent reviews on NHCs, see for examples: (a) T. Dröge and F. Glorius, Angew. Chem., Int. Ed., 2010, 49, 6940; (b) G. C. Vougioukalakis and R. H. Grubbs, Chem. Rev., 2010, 110, 1746; (c) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, Chem. Rev., 2009, 109, 3561; (d) P. L. Arnold and I. J. Casely, Chem. Rev., 2009, 109, 3599; (e) S. Díez-González, N. Marion and S. P. Nolan, Chem. Rev., 2009, 109, 3612; (f) M. Poyatos, J. A. Mata and E. Peris, Chem. Rev., 2009, 109, 3677; (g) C. Samojłowicz, M. Bieniek and K. Grela, Chem. Rev., 2009, 109, 3708; (h) W. A. L. van Otterlo and C. B. de Koning, Chem. Rev., 2009, 109, 3743; (i) S. Monfette and D. E. Fogg, Chem. Rev., 2009, 109, 3783; (j) B. Alcaide, P. Almendros and A. Luna, Chem. Rev., 2009, 109, 3817; (k) F. E. Hahn and M. C. Jahnke, Angew. Chem., Int. Ed., 2008, 47, 3122; (1) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, Chem. Rev., 2000, 100, 39.

- 4 For recent books on NHCs, see: (a) N-Heterocyclic Carbenes, From laboratory Curiosities to Efficient Synthetic Tools, ed. S. Díez-González, Royal Society of Chemistry Publishing, 2011; (b) N-Heterocyclic Carbenes in Transition Metal Catalysis, ed. F. A. Glorius, Springer Verlag, 2007; (c) N-Heterocyclic Carbenes in Synthesis, ed. S. P. Nolan, Wiley-VCH, 2006.
- 5 (a) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, 326, 556; (b) G. Ung and G. Bertrand, *Chem.-Eur. J.*, 2011, 17, 8269; (c) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2010, 132, 14370.
- 6 (a) V. Lavallo, C. A. Dyker, B. Donnadieu and G. Bertrand, Angew. Chem., Int. Ed., 2008, 47, 5411; (b) I. Fernández, C. A. Dyker, A. DeHope, B. Donnadieu, G. Frenking and G. Bertrand, J. Am. Chem. Soc., 2009, 131, 11875.
- 7 (a) G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, Angew. Chem., Int. Ed., 2010, 49, 4759;
  (b) J. Bouffard, B. K. Keitz, R. Tonner, G. Guisado-Barrios, G. Frenking, R. H. Grubbs and G. Bertrand, Organometallics, 2011, 30, 2617; (c) B. K. Keitz, J. Bouffard, G. Bertrand and R. H. Grubbs, J. Am. Chem. Soc., 2011, 133, 8498.
- 8 For the origin of the acronym MIC, see: S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto, K. Chiba and Y. Butsugan, *Chem. Ber.*, 1993, **126**, 1149.

- 9 (a) G. Ung, D. Mendoza-Espinosa, J. Bouffard and G. Bertrand, *Angew. Chem., Int. Ed.*, 2011, **50**, 4215; (b) G. Ung, G. D. Frey, W. W. Schoeller and G. Bertrand, *Angew. Chem., Int. Ed.*, 2011, DOI: 10.1002/anie.201104303.
- 10 A. Dehope, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, Angew. Chem., Int. Ed., 2007, 46, 6922.
- See for recent examples: (a) K. Hirano, A. T. Biju, I. Piel and F. Glorius, J. Am. Chem. Soc., 2009, 131, 14190; (b) R. Lebeuf, K. Hirano and F. Glorius, Org. Lett., 2008, 10, 4243; (c) A. T. Biju and F. Glorius, Angew. Chem., Int. Ed., 2010, 49, 9761; (d) I. Piel, M. Steinmetz, K. Hirano, R. Frohlich, S. Grimme and F. Glorius, Angew. Chem., Int. Ed., 2011, 50, 4983.
- 12 R. Breslow, J. Am. Chem. Soc., 1958, 80, 3719.
- 13 A. J. Arduengo, III, J. R. Goerlish and W. J. Marshal, *Liebigs Ann./Recl.*, 1997, 365.
- 14 (a) P. Mathew, A. Neels and M. Albrecht, J. Am. Chem. Soc., 2008, 130, 13534; (b) A. John, M. M. Shaik and P. Ghosh, Dalton Trans., 2009, 10581; (c) X. Xu, B. Xu, Y. Li and S. H. Hong, Organometallics, 2010, 29, 6343.
- 15 D. Tapu, D. A. Dixon and C. Roe, Chem. Rev., 2009, 109, 3385.
- 16 A. Fürstner, M. Alcarazo, H. Krause and C. W. Lehmann, J. Am. Chem. Soc., 2007, 129, 12676.
- 17 V. Lavallo, Y. Canac, A. Dehope, B. Donnadieu and G. Bertrand, Angew. Chem., Int. Ed., 2005, 44, 7236.