

# A simple, general route to 2-pyridylidene transition metal complexes†

Marta Roselló-Merino,<sup>a</sup> Josefina Díez<sup>b</sup> and Salvador Conejero<sup>\*a</sup>

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

5 DOI: 10.1039/b000000x

Pyridinium 2-carboxylates decompose thermally in the presence of a variety of late transition metal precursors to yield the corresponding 2-pyridylidene-like complexes. The mild reaction conditions and structural diversity that can be generated in the heterocyclic ring makes this method an attractive alternative for the synthesis of 2-pyridylidene complexes. IR spectra of the Ir(I) carbonyl compounds [IrCl(NHC)(CO)<sub>2</sub>] indicate that these N-heterocyclic carbene ligands are among the strongest σ-electron donors.

15 The importance of N-heterocyclic carbenes (NHCs) as ligands for transition metal complexes and catalysis is nowadays well established.<sup>1</sup> Arduengo's type NHCs have been intensively explored, but in the last few years new structures based on nitrogen-containing heterocycles have been synthesized, either in their free form or coordinated to transition metals.<sup>1e,j,2</sup> Among them, those stabilized by a single heteroatom have been targeted due to their superior electron donor properties in comparison with classical NHCs.<sup>1j,3</sup> Pyridylidene-like derivatives I, II and III (Figure 1) are of special interest since, in addition to their excellent σ-donor properties they can behave as good π-acceptors towards transition metals.<sup>4</sup>

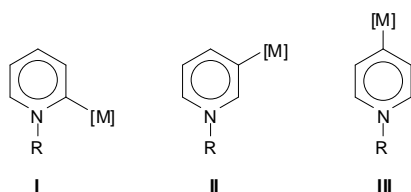


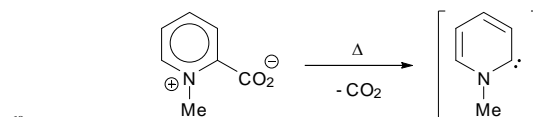
Fig. 1 2-, 3- and 4-pyridylidene complexes.

30 Carbene compounds of these types have long been known<sup>5</sup> and have been generated by various synthetic procedures that include: N-functionalization of pyridyl derivatives;<sup>6</sup> oxidative addition of pyridinium halides to metal complexes;<sup>7</sup> C–H bond activation of pyridinium salts;<sup>8</sup> tautomerization processes of pyridines to N-heterocyclic carbenes mediated by transition metals;<sup>9</sup> cycloaddition reactions to Fischer type carbenes;<sup>10</sup> and transmetalation reactions.<sup>11</sup> Although these methods may be employed in particular instances, they lack generality and moreover suffer from important drawbacks: increase in the metal oxidation state; availability of the starting materials, etc. Deprotonation of pyridinium salts has been reported recently, but the scope of this procedure is still limited to the synthesis of some ruthenium clusters.<sup>12</sup>

Herein, we report a new, widely applicable synthetic approach to 2-pyridylidene complexes that makes use of an old concept: decarboxylation of pyridinium carboxylates.

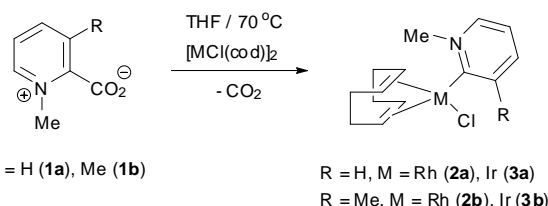
Crabtree *et al.* have recently reported a similar method for the synthesis of Arduengo's type NHCs complexes.<sup>13</sup>

Some seventy years ago Hammick *et al.* observed that pyridine-2-carboxylic acid (*i.e.* 2-picolinic acid) undergoes decarboxylation with greater facility than its 3- and 4-isomers, due to the intermediacy of the 2-ylide (or 2-carbene) isomer of pyridine.<sup>14</sup> It was subsequently found<sup>15,16</sup> that N-alkylated pyridinium 2-carboxylates release CO<sub>2</sub> more than 700 times faster than 2-picolinic acid (Scheme 1). Since the resulting carbene intermediates can be trapped by electrophiles and may be used for the low temperature synthesis (60–80 °C) of pyridinium salts,<sup>17</sup> we reasoned that betaines of this kind could be employed as precursors for transition metal carbenes.



Scheme 1 Decarboxylation of an N-methylated pyridinium 2-carboxylate.

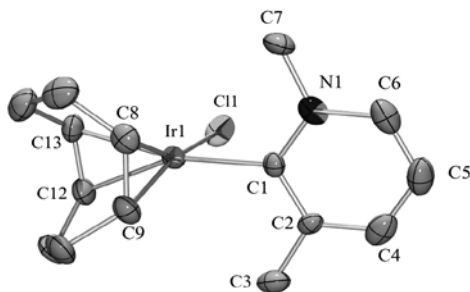
Aiming to prove this hypothesis, N-methyl-2-carboxypyridinium betaine **1a** (commonly known as homarine<sup>18</sup>) has been synthesized (Scheme 2) and decomposed thermally in the presence of [RhCl(cod)]<sub>2</sub>, under strictly anhydrous conditions. Gratifyingly, a smooth reaction was observed leading to complex **2a** in *ca.* 90% yield (by NMR spectroscopy), contaminated with very small amounts of the corresponding pyridinium salt, resulting from action of adventitious water on the transient N-heterocyclic carbene. No signal due to the –CO<sub>2</sub><sup>–</sup> group of the starting material can be found in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2a**, and furthermore a deshielded resonance is detected at 216 ppm, that features a coupling of 43 Hz to the <sup>103</sup>Rh nucleus. Both the chemical shift of the carbenic carbon atom and its coupling with the <sup>103</sup>Rh nucleus support a metal-carbene formulation.<sup>19</sup> Thus, CO<sub>2</sub> is released during the reaction and the resulting NHC unit becomes bonded to the rhodium center.



Scheme 2 Decarboxylation of betaines **1a** and **1b** in the presence of rhodium and iridium complexes.

Decarboxylation of **1a** also occurs in the presence of the analogous Ir(I) precursor, [IrCl(cod)]<sub>2</sub>, to produce complex

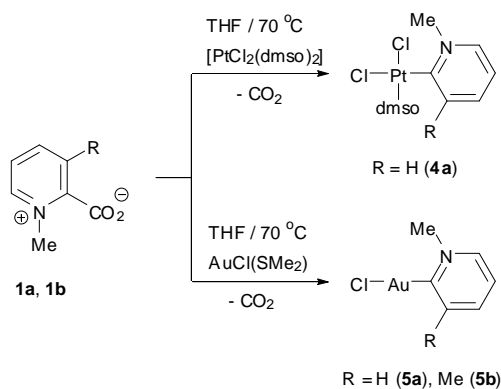
**3a**. Once more, the carbene carbon atom resonates as a singlet at  $\delta$  210. Related Rh and Ir complexes derived from 1,3-dimethylpyridinium-2-carboxylate, **1b**, (see Supporting Information) can also be made (compounds **2b** and **3b**, respectively, in Scheme 2). They exhibit spectroscopic properties akin to those of compounds **2a** and **3a**. Iridium derivative **3b** has been additionally characterized by X-ray crystallography. As can be seen in Figure 2, molecules of **3b** contain a pyridine-2-ylidene fragment characterized by an Ir—C1 distance of 2.05 Å. This falls in the range found for known iridium–NHC complexes.<sup>8d,9b,d-g,20</sup>



**Fig. 2** ORTEP drawing (30% probability) for complex **3b**. Selected bond lengths (Å) and angles (deg): Ir1—C1 = 2.050(5), C1—C2 = 1.383(8), C2—C4 = 1.363(9), C4—C5 = 1.364(12), C5—C6 = 1.359(12), C6—N1 = 1.375(9), C1—N1 = 1.398(8); C2—C1—N1 = 115.7(5).

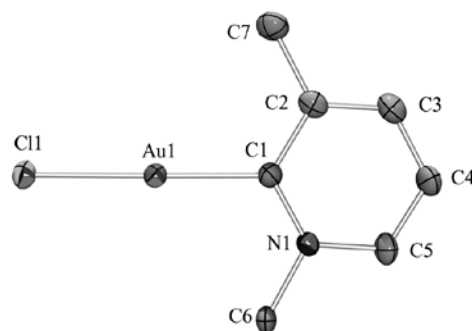
C—C and C—N bonds distances within the aromatic ring follow an irregular trend, in agreement with the carbene character of the heterocycle.<sup>2b</sup> It is clear from the above results that decarboxylation of pyridinium carboxylates such as **1b** permits selective synthesis of non-symmetrical 2-pyridylidenes that bear a substituent at the 3-position of the ring. This is in contrast with a hypothetical, alternative procedure consisting in deprotonation of 3-substituted pyridinium salts, as the latter route could give rise to either the 2- or the 6-pyridylidene, or a mixture of these two isomers due to the similar acidity of the C2—H and C6—H units.<sup>21</sup>

To extend the scope of the reaction and its applicability to other late transition metals, betaines **1a,b** have been reacted with complexes [PtCl<sub>2</sub>(dmsol)<sub>2</sub>] and [AuCl(SMe<sub>2</sub>)]. As shown in Scheme 3, the expected carbenes **4a** and **5a,b** have been isolated and characterized.<sup>22</sup>



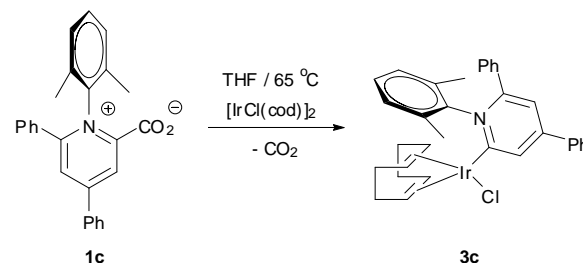
**Scheme 3** Decarboxylation of betaines **1a** and **1b** in the presence of platinum and gold complexes.

The solid-state structure of gold complex **5b** has been established by X-ray crystallography (Figure 3).



**Fig. 3** ORTEP drawing (30% probability) for complex **5b**. Selected bond lengths (Å) and angles (deg): Au1—C1 = 2.015(7), C1—C2 = 1.413(9), C2—C3 = 1.382(10), C3—C4 = 1.386(10), C4—C5 = 1.367(10), C5—N1 = 1.375(9), C1—N1 = 1.375(10); C2—C1—N1 = 118.7(6).

Extension to other pyridinium carboxylates, readily available by Katritzky's procedure,<sup>17b</sup> is also possible, introducing in this manner structural diversity on the pyridylidene framework. Thus, upon mild heating of betaine **1c** in the presence of [IrCl(cod)]<sub>2</sub> the expected NHC complex **3c** is formed (Scheme 4).



**Scheme 4** Decarboxylation of aryl-substituted betaine **1c** in the presence of [IrCl(cod)]<sub>2</sub>.

To evaluate the electron donor properties of these 2-pyridylidene ligands, carbonyl complexes [IrCl(NHC)(CO)<sub>2</sub>] (NHC = 1-methyl-2-pyridylidene, **6a**; 1,3-dimethyl-2-pyridylidene, **6b**) have been prepared by substitution of the *cod* ligand in complexes **3a,b**, respectively, by CO. The stretching frequencies of the C—O bonds appear at ca. 2060 and 1980 cm<sup>-1</sup> ( $\nu_{\text{average}} \sim 2020$  cm<sup>-1</sup>) in good agreement with values theoretically calculated recently by Gusev for nickel carbonyl complexes.<sup>23</sup> This experimental observation situates 2-pyridylidene ligands between the strongly electron donating abnormal-NHCs ( $\nu_{\text{average}} \sim 2005$  cm<sup>-1</sup>)<sup>3e</sup> and imidazol-2-ylidenes ( $\nu_{\text{average}} \sim 2022$ –2030 cm<sup>-1</sup>),<sup>[24]</sup> and makes them comparable to the recently reported 1,2,3-triazolylidenes.<sup>3b,e</sup>

In summary, we have developed a new and efficient method for the synthesis of 2-pyridylidene complexes based on decarboxylation of pyridinium carboxylates that opens new possibilities in the chemistry of these almost unexplored carbene ligands.

We thank the Junta de Andalucía (project No. FQM-3151) and MICINN (Spain) (projects CTQ2007-62814 and

CONSOLIDER-INGENIO 2010 CSD2007-00006, FEDER support) for financial support. M.R. thanks the CSIC for a JAE grant. The authors also thank Prof. Ernesto Carmona for valuable comments and continuous support.

## 5 Notes and references

<sup>a</sup> Instituto de Investigaciones Químicas, Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas, Universidad de Sevilla, Avda. Américo Vespucio 49, Sevilla, 41092, Spain. Fax: +34 954460565; Tel: +34 954489563; E-mail: sconejero@iiq.csic.es

<sup>b</sup> Departamento de Química Orgánica e Inorgánica Universidad de Oviedo, C/ Julián Clavería 8, 33006, Oviedo, Spain.

† Electronic Supplementary Information (ESI) available: Full experimental procedures and data. CCDC 791629 (**3b**), 791630 (**5b**). See DOI: 10.1039/b000000x/

- 1 (a) D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39. 8b) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, **41**, 1290. (c) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247. (d) F. Glorius, *Top. Organomet. Chem.*, 2007, **21**, 1. e) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122. (f) A. T. Normand and K. J. Cavell, *Eur. J. Inorg. Chem.*, 2008, 2781. (g) 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. (h) P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, **109**, 3599. i) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676. j) M. Melaime, M. Soleilhavou and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, DOI: 10.1002/anie.201000165.
- 2 (a) P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596. (b) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445.
- 3 (a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2005, **44**, 5705. (b) P. Mathew, A. Neels and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 13534. (c) E. Aldecoperez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, **326**, 556. (d) M. Iglesias and M. Albrecht, *Dalton Trans.*, 2010, 5213. (e) G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2010, **49**, 4759.
- 4 (a) R. G. Raubenheimer and S. Cronje, *Dalton Trans.*, 2008, 1265. (b) A. A. Tukov, A. T. Normand and M. S. Nechaev, *Dalton Trans.*, 2009, 7015.
- 5 P. J. Fraser, W. R. Roper and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 760.
- 6 H. G. Raubenheimer, J. G. Toerien, G. J. Kruger, R. Otte, W. van Zyl and P. Olivier, *J. Organomet. Chem.*, 1994, **466**, 291.
- 7 (a) U. Kirchgässner, H. Piana and U. Schubert, *J. Am. Chem. Soc.* 1991, **113**, 2228. (b) S. K. Schneider, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking and W. A. Herrmann, *Dalton Trans.*, 2006, 1226. (c) A. Poulain, A. Neels and M. Albrecht, *Eur. J. Inorg. Chem.*, 2009, 1871.
- 8 (a) J. S. Owen, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.* 2004, **126**, 8247. (b) M. Albrecht and H. Stoeckli-Evans, *Chem. Commun.*, 2005, 4705. (c) C. P. Newman, G. J. Clarkson, N. W. Alcock and J. P. Rourke, *Dalton Trans.*, 2006, 3321. (d) G. Song, Y. Zhang, Y. Su, W. Deng, K. Han and X. Li, *Organometallics*, 2008, **27**, 6193.
- 9 (a) R. Cordone and H. Taube, *J. Am. Chem. Soc.*, 1987, **109**, 8101. (b) E. Alvarez, S. Conejero, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano and E. Carmona, *J. Am. Chem. Soc.*, 2006, **128**, 13060. (c) M. A. Esteruelas, F. J. Fernández-Alvarez and E. Oñate, *J. Am. Chem. Soc.*, 2006, **128**, 13044. (d) E. Alvarez, S. Conejero, P. Lara, J. A. López, M. Paneque, A. Petronilho, M. L. Poveda, D. del Río, O. Serrano and E. Carmona, *J. Am. Chem. Soc.*, 2007, **129**, 14130. (e) S. Conejero, P. Lara, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano, F. Vattier, E. Alvarez, C. Maya, V. Salazar and E. Carmona, *Angew. Chem. Int. Ed.*, 2008, **47**, 4380. (f) M. Paneque, M. L. Poveda, F. Vattier, E. Alvarez and E. Carmona, *Chem. Commun.* 2009, 5561. (g) E. Alvarez, Y. A. Hernández, J. López-Serrano, C. Maya, M. Paneque, A. Petronilho, M. L. Poveda, V. Salazar, F. Vattier and E. Carmona, *Angew. Chem. Int. Ed.*, 2010, **49**, 3496.
- 10 (a) R. Aumann and P. Hinterding, *Chem. Ber.*, 1992, **125**, 2765. (b) C. Gimenez, N. Luga, R. Mathieu and G. L. Geoffroy, *J. Organomet. Chem.*, 1996, **517**, 133.
- 11 C. E. Strasser, E. Stander-Glober, O. Schuster, S. Cronje and H. G. Raubenheimer, *Eur. J. Inorg. Chem.*, 2009, 1905.
- 12 J. A. Cabeza, I. del Río, E. Pérez-Carreño, M. G. Sánchez-Vega and D. Vázquez-García, *Angew. Chem. Int. Ed.*, 2009, **48**, 555.
- 13 (a) A. M. Voutchkova, L. N. Appelhans, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.*, 2005, **127**, 17624. (b) A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 2007, **129**, 12834.
- 14 (a) P. Dyson and D. L. Hammick, *J. Chem. Soc.*, 1937, 1724. (b) M. R. F. Ashworth, R. P. Daffern and D. L. Hammick, *J. Chem. Soc.*, 1939, 809.
- 15 B. R. Brown and D. L. Hammick, *J. Chem. Soc.*, 1949, 659.
- 16 P. Haake and J. Mantecón, *J. Am. Chem. Soc.*, 1964, **86**, 5230.
- 17 (a) H. Quast and E. Frankenfeld, *Angew. Chem. Int. Ed. Engl.*, 1965, **4**, 691. (b) A. R. Katritzky, R. Awartani and R. C. Patel, *J. Org. Chem.*, 1982, **47**, 498. (c) A. R. Katritzky and H. M. Faid-Allah, *Synthesis*, 1983, 149. (d) A. R. Katritzky, W. -K. Yeung, A. J. Cozens and O. Rubio, *J. Chem. Soc., Perkin Trans. I*, 1985, 2159. (e) A. R. Katritzky, A. J. Cozens, A. Ossana, O. Rubio and N. Dabbas, *J. Chem. Soc., Perkin Trans. I*, 1985, 2167.
- 18 H. Quast, E. Schmitt, *Liebigs Ann. Chem.*, 1970, **732**, 64.
- 19 F. P. Fanizzi, G. J. Sunley, J. A. Wheeler, H. Adams, N. A. Bailey and P. M. Maitlis, *Organometallics*, 1990, **9**, 131.
- 20 (a) A. S. Ionkin, W. J. Marshall, D. C. Roe and Y. Wang, *Dalton Trans.*, 2006, 2468. (b) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677.
- 21 O. Hollóczki and L. Nyulászi, *J. Org. Chem.*, 2008, **73**, 4794.
- 22 For unclear reasons, we have not succeeded yet in the isolation of compound **4b** (R = Me).
- 23 D. G. Gusev, *Organometallics*, 2009, **28**, 6458.