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

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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 make this method an attractive alternative for the synthesis of 2-pyridylidene complexes. IR spectra of the Ir(ı) carbonyl compounds [IrCl(NHC)(CO)$_2$] indicate that these N-heterocyclic carbene ligands are among the strongest σ-electron donors.

The importance of N-heterocyclic carbenes (NHCs) as ligands for transition metal complexes and catalysis is nowadays well established.[1] 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.[1e,j,2] Among them, those stabilized by a single heteroatom have been targeted due to their superior electron donor properties in comparison with classical NHCs.[1j,3] Pyridylidene-like derivatives I, II and III (Fig. 1) are of special interest since, in addition to their excellent σ-donor properties, they can behave as good π-acceptors towards transition metals.[4]

Carbene compounds of these types have long been known[5] and have been generated by various synthetic procedures that include: N-functionalization of pyridyl derivatives;[6] oxidative addition of pyridinium halides to metal complexes;[7] C–H bond activation of pyridinium salts;[8] tautomerization processes of pyridines to N-heterocyclic carbenes mediated by transition metals;[9] cycloaddition reactions to Fischer type carbenes;[10] and transmetalation reactions.[11] 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.[12]

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.[13]

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.[14] It was subsequently found[15,16] that N-alkylated pyridinium 2-carboxylates release CO_2 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,[17] we reasoned that betaines of this kind could be employed as precursors for transition metal carbenes.

Aiming to prove this hypothesis, *N*-methyl-2-carboxy-pyridinium betaine **1a** (commonly known as homarine)[18] has been synthesized (Scheme 2) and decomposed thermally in the presence of [RhCl(cod)]$_2$, *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 the action of adventitious water on the transient N-heterocyclic carbene. No signal due to the –CO_2^- group of the starting material can be found in the $^{13}C\{^1H\}$ NMR spectrum of **2a**, and furthermore a deshielded resonance is detected at 216 ppm, that features a coupling of 43 Hz to the ^{103}Rh nucleus. Both the chemical shift of the carbenic carbon atom and its coupling with the ^{103}Rh
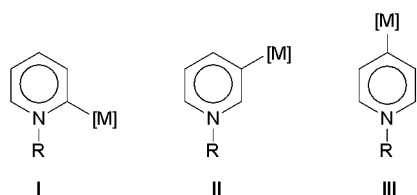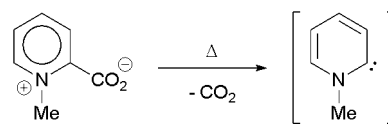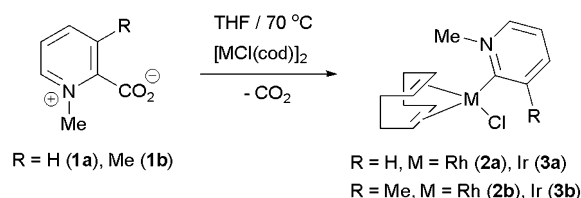

Fig. 1 2-, 3- and 4-pyridylidene complexes.

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

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

nucleus support a metal–carbene formulation.[19] Thus, CO_2 is released during the reaction and the resulting NHC unit becomes bonded to the rhodium center.

Decarboxylation of **1a** also occurs in the presence of the analogous Ir(I) precursor, [IrCl(cod)]$_2$, to produce complex **3a**. Once more, the carbene carbon atom resonates as a singlet at δ 210. Related Rh and Ir complexes derived from 1,3-dimethyl-pyridinium-2-carboxylate, **1b** (see ESI†), 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 Fig. 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.[8d,9b,d–g,20]

The C–C and C–N bond distances within the aromatic ring follow an irregular trend, in agreement with the carbene character of the heterocycle.[2b] It is clear from the above results that decarboxylation of pyridinium carboxylates such as **1b** permits a selective synthesis of non-symmetrical 2-pyridyl-idenes 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.[21]

To extend the scope of the reaction and its applicability to other late transition metals, betaines **1a,b** have been reacted with complexes [PtCl$_2$(dmso)$_2$] and [AuCl(SMe$_2$)]. As shown in Scheme 3, the expected carbenes **4a** and **5a,b** have been isolated and characterized.[22]

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

Extension to other pyridinium carboxylates, readily available by Katritzky's procedure,[17b] 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)]$_2$ the expected NHC complex **3c** is formed (Scheme 4).

To evaluate the electron donor properties of these 2-pyridylidene ligands, carbonyl complexes [IrCl(NHC)(CO)$_2$] (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

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

Fig. 3 ORTEP drawing (30% probability) for complex **5b**. Selected bond lengths (Å) and angles (°): 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).

Scheme 4 Decarboxylation of aryl-substituted betaine **1c** in the presence of [IrCl(cod)]$_2$.

stretching frequencies of the C–O bonds appear at *ca.* 2060 and 1980 cm^{-1} ($\nu_{average} \approx 2020$ cm^{-1}) in good agreement with the values theoretically calculated recently by Gusev for nickel carbonyl complexes.[23] This experimental observation situates 2-pyridylidene ligands between the strongly electron donating abnormal-NHCs (*a*NHCs) ($\nu_{average} \approx 2005$ cm^{-1})[3e] and imidazol-2-ylidenes ($\nu_{average} \approx 2022$–2030 cm^{-1}),[24] and makes them comparable to the recently reported 1,2,3-triazol-ylidenes.[3b,e]

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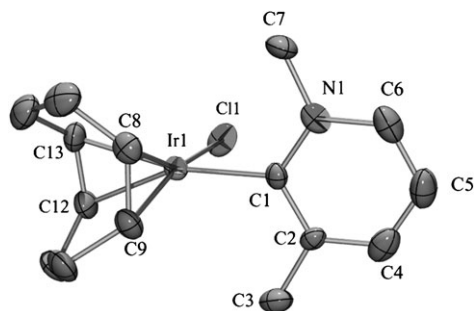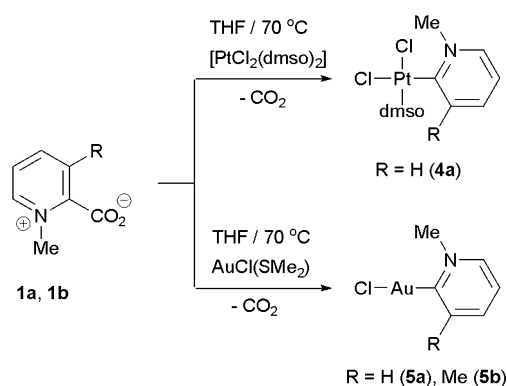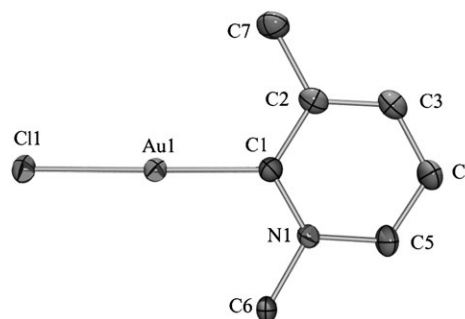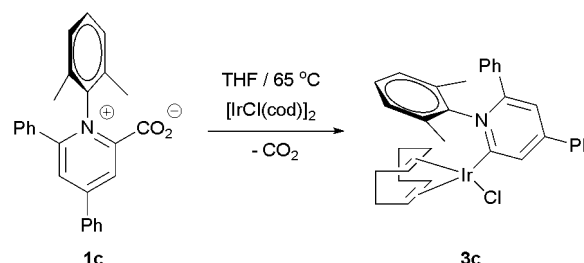
Fig. 2 ORTEP drawing (30% probability) for complex **3b**. Selected bond lengths (Å) and angles (°): Ir1–C1 = 2.050(5), C1–C2 = 1.383(8), C2–C4 = 1.363(9), C4–C5 = 1.364(12), C5–C6 = 1.359(12), C6–N1 = 1.375(9), C1–N1 = 1.398(8); C2–C1–N1 = 115.7(5).

Notes and references

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