Unexpected reduction pathway of a Co^{2+} salt to $[HCo(CO)_4]$ *via* $[Co_2(CO)_8]$ in an ionic liquid†‡

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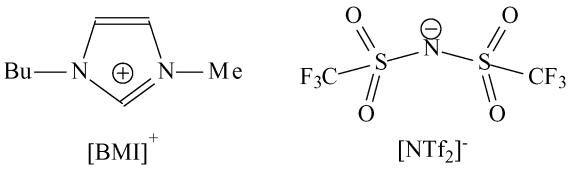
In the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquid ([BMI][NTf$_2$]), [Co(NTf$_2$)$_2$] is reduced under 5.5 MPa of H_2–CO to $[Co_2(CO)_8]$ prior to $[HCo(CO)_4]$, provided a pyridine ligand is present in the medium.

It is usually very difficult to clearly determine the exact mechanisms occurring during a catalytic cycle, more especially in the case of short-lived species. For this purpose, operating spectroscopic observations under catalytic conditions is certainly a powerful method, since intermediate species can be evidenced, and infrared spectroscopy appears as a very suitable tool for reactions involving carbonyl complexes. In the course of industrial hydroformylation involving cobalt catalysts, it is known that the generation of neutral carbonyl complexes can be achieved starting from almost all cobalt forms in their +II, +III oxidation states and even from metallic powder. Among these Co(II) salts, mainly cobalt carboxylates, play an important role as they are introduced as precursors and are also formed during recycling steps. In these processes, the generation of cobalt carbonyl active species requires high pressures, as high as 20 MPa, and 150 to 200 °C.[1]

In order to combine the catalytic activity of cobalt with an efficient recycling process, the hydroformylation of alkenes was recently performed at 10 MPa in the presence of a {cobalt–pyridine–ionic liquid} system. The ionic liquid which has been shown to deliver the most promising results[2] was 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [BMI][NTf$_2$] (Scheme 1).



Scheme 1 Formula of [BMI][NTf$_2$].

It is already well established that pyridine (py) leads to the disproportionation of $[Co_2(CO)_8]$ (**1**) into the Co(II)/Co(−I) salt $[Co(py)_6][Co(CO)_4]_2$ (**2**).[3] Earlier studies have evidenced that **2** is slowly transformed under ambient conditions by a H_2–CO mixture into $[pyH][Co(CO)_4]$ (**3**).[4] The pyridinium salt is in equilibrium with the hydride $[HCo(CO)_4]$ (**4**) and pyridine according to eqn (1).

$$\underset{\mathbf{3}}{[pyH][Co^{-I}(CO)_4]} \rightleftharpoons \underset{\mathbf{4}}{[HCo^{I}(CO)_4]} + py \qquad (1)$$

We were particularly interested in the mode of reduction of the $[Co(py)_6]^{2+}$ cobalt(II) species involved in these systems and in the process generating **4**. For that purpose, the reaction of **2** with H_2–CO was followed in heptane in a HP-IR cell[5] at 5.5 MPa[6] by varying the temperature. Under these conditions, no particular change could be detected for the broad and intense T_2 ν_{CO} band at 1889 cm^{-1}, characteristic of the anion $[Co(CO)_4]^-$. Conversely, the appearance of **4** and the pyridium cation $[pyH]^+$ was observed (band at 1633 cm^{-1}). In addition, free pyridine is also present in the organic phase as shown by the presence of two bands at 1595 (w) and 1578 (m) cm^{-1}. The overall equation for this reaction is consistent with the reduction of the cobalt(II) centre of **2** into the cobalt(−I) species (**3**).

$$\underset{\mathbf{2}}{[Co(py)_6][Co(CO)_4]_2} \xrightleftharpoons{H_2-CO} 3\ \underset{\mathbf{3}}{[pyH][Co(CO)_4]} + 3py \qquad (2)$$

In order to gain more insight into the reduction path of cobalt(II) species, we examined, again using infrared spectroscopy at 5.5 MPa, at variable temperatures, the fate of $[Co^{II}(NTf_2)_2]$ (**5**) dissolved in the ionic liquid [BMI][NTf$_2$] in the presence of heptane under a 1 : 1 H_2–CO mixture. Salt **5** was prepared by addition of two equivalents of the acid HNTf$_2$ to a suspension of cobalt carbonate in water.[7] The resulting pale pink solid was dissolved at room temperature in [BMI][NTf$_2$]. This solution and heptane were introduced in the HP-IR cell, and the mixture was stirred efficiently to avoid gas–liquid transfer limitations. The pressure was maintained at 5.5 MPa in order to fit the stability range of the neutral carbonyl cobalt complexes, described for the classical hydroformylation process.[1b] Before recording the spectra, the system was allowed to equilibrate for 30 min for each observation temperature. Heating in the absence of pyridine at successively 40, 60, 80, 100, 120, 130 and 140 °C (total duration 3.5 h) did not result in any ν_{CO} band detection and, even after maintaining the temperature for a further 2 h, no carbonyl complex could be detected. Conversely, when adding 2 molar equivalents of pyridine to **5**, and heating under the same conditions and in the same way allowed us to observe ν_{CO} bands above 120 °C. Fig 1 shows the spectrum at 120 °C (Fig. 1b) with only the basal line and that recorded at 130 °C (Fig. 1c) which reveals the typical ν_{CO} bands of **1** at 2112 (w), 2066 (s), 2054 (sh), 2041 (s), 2031 (s), 2024 (s) for the terminal CO ligands and at 1867 (m) and 1861 (m) cm^{-1} for the bridging CO ligands.[8] At 140 °C (see Fig. 1d and Fig. 2) significant changes occurred, the concentration of **1** dramatically decreased (2068, 2041 and 2023 cm^{-1} clearly identified) and small

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Spectra of $[HCo(CO)_4]$ and $[Co_2(CO)_8]$ (solutions in heptane), recorded in the HP-IR cell. See DOI: 10.1039/b616169n

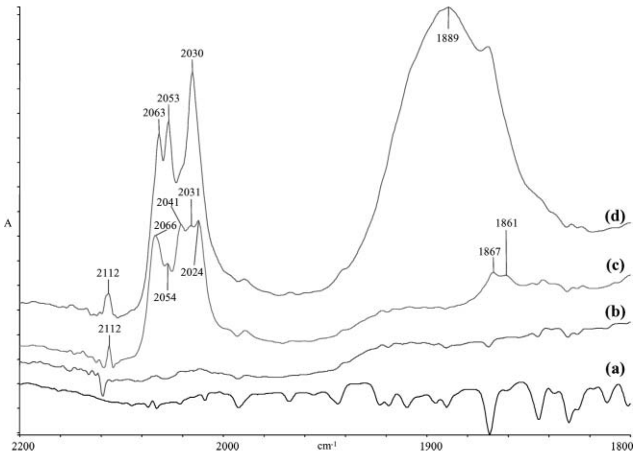

Fig. 1 IR spectra (ν_{CO} region) for the [Co(NTf$_2$)$_2$]–Py–[BMI][NTf$_2$] system evolution under H_2–CO pressure, varying the temperature. (a) 1 MPa, 40 °C; (b) 5 MPa, 120 °C; (c) 5.5 MPa, 130 °C; (d) 5.5 MPa , 140 °C.

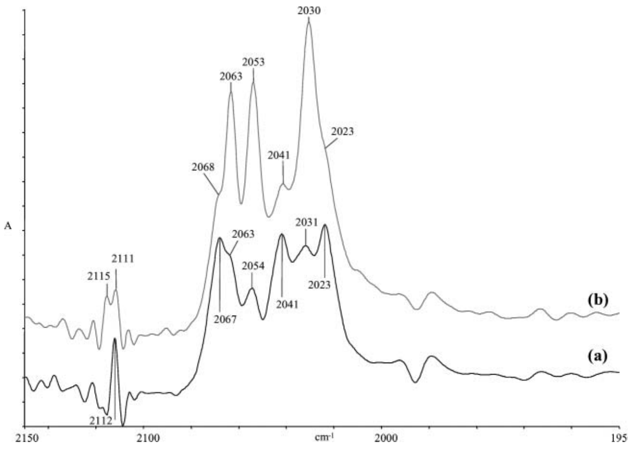

Fig. 2 Deconvolution spectra for the produced carbonyl species (c and d, Fig. 1) starting from [Co(NTf$_2$)$_2$]–Py–[BMI][NTf$_2$]. (a) Treatment as in Fig. 1c (5.5 MPa, 130 °C); (b) treatment as in Fig. 1d (5.5 MPa, 140 °C).

amounts (based on the relative intensities) of [Co(CO)$_4$]$^-$ appeared at 1889 cm^{-1}; the two ν_{CO} bands at 2053 (s) and 2030 (vs) cm^{-1} can be ascribed to the formation of a significant amount of **4**. Deconvolution of the spectra at 130 and 140 °C (Fig. 2)[9] evidenced the presence of a band at 2115 cm^{-1}, which confirms the presence of **4**. It is worth noting that some [Co$_4$(CO)$_{12}$] (**6**) is present in the solution, presumably in equilibrium with **1** and characterized by the two bands at 2063 (s) and 2053 (s) cm^{-1}, and the shoulder at 1868 cm^{-1}.

Thus, under H_2–CO pressure, above 130 °C, the reduction of [Co(NTf$_2$)$_2$] in the presence of pyridine occurs to give first the cobalt(0) complex [Co$_2$(CO)$_8$] (and some [Co$_4$(CO)$_{12}$] as well). Further heating produces [HCo(CO)$_4$] and [PyH][Co(CO)$_4$], due to the equilibrium of eqn (1) governed by temperature.

When using a classical salt such as CoCl$_2$, we observed that in order to form [Co(CO)$_4$]$^-$, it is necessary to add pyridine to the medium. Observations, by HP-IR, of the reduction of CoCl$_2$ in [BMI][NTf$_2$] were carried out in the presence of 6 equivalents of pyridine. The progressive formation of the anion [Co(CO)$_4$]$^-$ is clearly evidenced above 120 °C, at 5.5 MPa, and the overall reduction scheme is summarized in eqn (3).

$$\mathrm{CoCl_2, 6\,py} \xrightarrow[\text{[BMI][NTf}_2\text{]}]{H_2-CO} \underset{\mathbf{3}}{\mathrm{[pyH][Co(CO)_4]}} + \mathrm{2[pyH]Cl + 3\,py} \qquad (3)$$

In conclusion, cobalt(II) salts, at 5.5 MPa and 130 °C, can be reduced in an ionic liquid by H_2–CO to carbonyl species, provided that pyridine is added. The two cobalt(0) complexes, namely [Co$_2$(CO)$_8$] and [Co$_4$(CO)$_{12}$], appear first before being transformed into [HCo(CO)$_4$]. Such a Co(II)–Co(0) sequence, which co-produces a pyridinium cation, should involve a heterolytic activation process of H_2 favoured by the presence of the ionic liquid medium. Indeed, in the previous work carried out by Lee and Kochi,[10] it has been shown that for the dismutation and reformation of [Co$_2$(CO)$_6$(PPh$_3$)$_2$], the addition of a salt inhibits the radical processes.

Notes and references

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5 The HP-IR cell is built from a Top Industrie HB2 autoclave of 45 mL volume, with mechanical stirring and equipped with a Rushton-type turbine. The IR beam of a Perkin Elmer GX FT-IR spectrometer is focused on a monocrystalline silicon rod and refocused beyond the reactor on the detector through a Cassegrain lens.
6 [Co$_2$(CO)$_8$]: 6.3 mmol; Py: 2 eq per Co; heptane: 20 mL.
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