

### Preliminary communication

## DIHYDROGEN ACTIVATION PROMOTED BY HOMONUCLEAR ION PAIRS INVOLVING COBALT(II) AND COBALT(–I)

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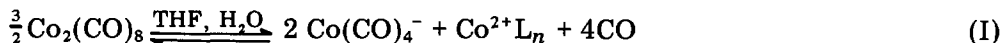
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### Summary

Acyltetracarbonyls have been shown to be formed from the reaction of hexene with CO/H<sub>2</sub> (1/1) mixtures ( $P(\text{CO}) = P(\text{H}_2) = 300$  mmHg) in THF/H<sub>2</sub>O at room temperature catalysed by homonuclear Co<sup>II</sup>, Co<sup>–I</sup> ion pairs.

We recently showed that the disproportionation of Co<sub>2</sub>(CO)<sub>8</sub> in THF occurs only in the presence of water (eq. 1) [1].



(L = H<sub>2</sub>O, THF, Co(CO)<sub>4</sub><sup>–</sup>, bound through oxygen atom)

Under suitable conditions, Co(CO)<sub>4</sub><sup>–</sup> competes with water and THF for the coordination sphere of Co<sup>2+</sup> and we observed ion pairing phenomena in these solutions [1]. Since the same transition metal is present in both anion and cation, we refer to interaction "homonuclear ion pairing". The reversibility of reaction 1 was interpreted in terms of such homonuclear ion pairing, which allows CO-mediated electron transfer from Co(CO)<sub>4</sub><sup>–</sup> to Co<sup>2+</sup> to occur. The relevance of these observations to a better understanding of dihydrogen activation promoted by cobalt carbonyls is revealed by the new observation, reported here, that syngas absorption and formation of acylcobalt tetracarbonyls, C<sub>7</sub> aldehydes and C<sub>13</sub> ketones from 1-hexene occur at room temperature and atmospheric pressure when homonuclear ion pairing equilibria between Co<sup>2+</sup> and Co(CO)<sub>4</sub><sup>–</sup> are operating.

A 0.03 M solution of Co<sub>2</sub>(CO)<sub>8</sub> in wet THF (30 ml) (H<sub>2</sub>O/Co<sub>2</sub>(CO)<sub>8</sub> molar ratio 2) was equilibrated with CO/H<sub>2</sub> 1/1 at 23°C under 1 atm of total pressure

$(P(\text{CO}) = P(\text{H}_2) = 300 \text{ mmHg})$ .

Upon addition of 4 ml of 1-hexene (32 mmol) gas absorption began, and the reaction was monitored for 198 h gasvolumetrically and by IR spectroscopy, and the organic products were determined by GC and GC/MS.

During the first 10 h gas absorption was relatively fast and it then settled at a constant rate (0.1 mmol/h) for the remaining 186 h of the observations. At the beginning CO was preferentially consumed, but subsequently CO/H<sub>2</sub> reacted in 1/1 ratio. The IR spectra of the solution showed that acylcobalt tetracarbonyls [2] (2104 m, 2042 vs, 2021 vs, 2001 m and 1710 w cm<sup>-1</sup>) were formed during the initial steps, and the absorptions due to other cobalt carbonyl species decreased correspondingly [1]. After 198 h, the concentration of acylcobalt tetracarbonyls slightly decreased, while the bands due to Co(CO)<sub>4</sub><sup>-</sup> in various environments increased, probably due to small amounts of water formed by aldehyde condensation. At 198 h, 1-hexene had reacted to give C<sub>7</sub> aldehydes (18% conversion, normal/branched/internal = 3.9/3.9/1), 2- and 3-hexenes (15%), C<sub>13</sub> ketones (8%, 5-methyldodecan-6-one/tridecan-7-one 1.2) and minor amounts of C<sub>7</sub> alcohols and 2-n-pentyl-2-nonenal. Over long reaction times, amounts of CO<sub>2</sub> were formed, suggesting that hydrogen atoms incorporated in the products can also come from water, through a water gas shift reaction.

Solutions of Co<sub>2</sub>(CO)<sub>8</sub> in anhydrous THF, or completely disproportionated solutions in THF containing more than 3% of H<sub>2</sub>O, which prevents ion pairing, do not promote the hydroformylation under these mild conditions.

The products of the reaction suggest [3] the intermediacy of HCo(CO)<sub>4</sub>, but this was never detected in our solutions. The reversibility of reaction 1 and the present observations prompt us to regard the Co<sup>2+</sup> involved in homonuclear ion pairing as a coordinatively unsaturated and electron deficient species, probably able to activate dihydrogen.

## References

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