

Carbonylates, Structures, Intermediates and Reactivities

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Topic: Ion pairs can be generated in liquid ammonia by direct reduction of neutral species with solutions of the alkali metals. From the resulting solutions, ammoniates with a high content of ammonia molecules of crystallization precipitate, which can be analyzed by special low-temperature single crystal X-ray techniques. In the systems studied so far, a whole range of different ion-paired structural arrangements has been observed. Next to nothing is known about the situation in the solutions themselves. The reduction of carbonyl compounds to carbonylates^{146–151} is a suitable model system for an in-depth structural study, as CO provides a good probe for NMR and IR and the charge of the anions can vary from -1 up to -4 . As our recent report on $[\text{Ni}(\text{CO})_3]^{2-}$ shows,^{P1/1} even new anions may be discovered.

Aim of the Project: To elucidate the processes and structures occurring during the reduction of carbonyl compounds with alkali metals in liquid ammonia.

For this goal, we will react a variety of carbonyl starting materials with the whole range of alkali metals. While Li, Na and in rare cases K are able to form homoleptic ammine complexes and thus achieve a degree of ion pair separation, the heavier alkali metals maintain close contacts to the anions. Not only homoleptic carbonyls are suited, as the use of $[\text{PPh}_3]_2\text{Ni}(\text{CO})_2$ for the synthesis of $[\text{Ni}(\text{CO})_3]^{2-}$ showed, analogous transformations with Pd and Pt will be explored. The conditions under which the reductions lead to polynuclear carbonylates like $[\text{Ni}_2(\text{CO})_6]^{2-}$ will be examined. For all variations of reagents and conditions, the relative endpoint of the reactions will be determined by the low-temperature single crystal X-ray analysis of the ammoniates which crystallize.

In solution, the reactions will be monitored via ^{13}C -NMR in collaboration with R. Gschwind and via vibrational spectroscopy in collaboration with P. Nürnberger. It will be especially interesting to investigate whether open shell anions $[\text{M}(\text{CO})_n]^{i-}$ resulting from primary single electron uptakes can be detected. For the vibrational spectroscopy, a special cooled titration glass apparatus will be built which allows the constant monitoring of the reduction process.^{152–155} In collaboration with the Bauer group the chemistry of silylium carbonylates will be explored.

Within this project, PhD students will receive training in advanced preparative techniques. They will learn how to perform X-ray analysis of extremely sensitive and thermolabile crystals. They will design and optimize a new apparatus for the titration monitoring. They will in general benefit from the interactions with the collaborators.

Connections within the RTG: PhD students will obtain a profound understanding of the synthesis and catalytic applications of ion pairs (Gschwind, Bauer) as well as of the necessary analytical tools (Gschwind, Nürnberger) and the theoretical background (Horinek).

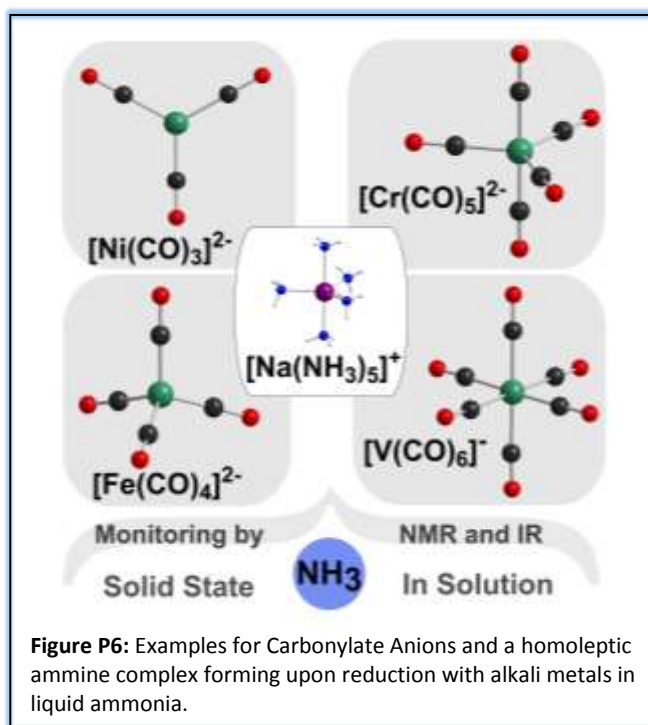


Figure P6: Examples for Carbonylate Anions and a homoleptic ammine complex forming upon reduction with alkali metals in liquid ammonia.