Doped Complex Bases, a New Consequence of Aggregative Activation

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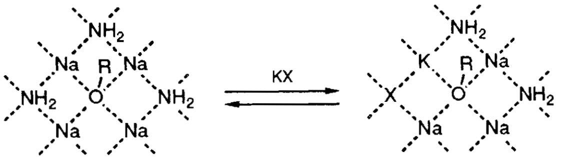
According to the basic principles of aggregative activation, it has been shown that the efficiency of the complex base $NaNH_2$–Bu^{t}ONa can be improved by simple addition of a potassium salt.

Sodium amide containing complex bases (CB) $NaNH_2$–RONa are useful reagents to generate carbanions and trigger anionic polymerisations as well as to perform *syn* eliminations or elimination–additions.[1] According to the basic principles of aggregative activation[2] CB properties may be easily modified by changing the nature of the activating agent RONa. These possibilities have been largely exploited.[1,2] Aggregative activation also leads to the expectation that the insertion of cations different from the ones included in a given CB should increase the aggregates dissymmetry and thus modify the efficiency of the bases. In the present publication we report the first results supporting this hypothesis. It is thus shown that it is possible to easily and inexpensively increase the efficiency of a CB by the simple addition of a salt. Taking into account that KNH_2 is a stronger base than $NaNH_2$,[3] we reasoned that a more efficient CB should be obtained by the insertion of K^+ into a sodium amide containing CB. The increase in efficiency was expected from the formation of aggregates containing species looking like complexed KNH_2 as shown in eqn. (1). To check this hypothesis we used, as previously,[4] the generation and condensation of the carbanions of Ph_nCH_{4-n} (n = 2, 3).

Doped complex bases (DCB) were prepared by addition of a dry potassium salt to a freshly formed classical CB ($NaNH_2$–Bu^{t}ONa, 2 equiv.: 1 equiv.) in tetrahydrofuran (THF) at 45 °C.[4] The suspension was stirred under nitrogen



(1)

Table 1 Alkylation of triphenylmethane and diphenylmethane by benzyl chloride in the presence of doped complex base (DCB)[a]

Entry	Substrates	KX	Equiv.	BRP/min[b]	Condensation product (%)[c]
1	Ph_3CH	None	—	65	99
2	Ph_3CH	KCl	1.5	30	99
3	Ph_3CH	KCl	1.0	25	99
4	Ph_3CH	KCl	0.15	30	99
5	Ph_3CH	KCl	0.10	75	99
6	Ph_3CH	KBr	1.5	25	99
7	Ph_3CH	KBr	0.15	60	99
8	Ph_3CH	KI	1.5	15	99
9	Ph_3CH	KI	0.15	15	99
10	Ph_3CH	$K_2C_2O_4$	1.5	25	99
11	Ph_2CH_2	None	—	135	90
12	Ph_2CH_2	KCl	1.5	25	79
13	Ph_2CH_2	KCl	0.15	25	79
14	Ph_2CH_2	KBr	1.5	20	82
15	Ph_2CH_2	KBr	0.15	75	82
16	Ph_2CH_2	KI	1.5	20	75
17	Ph_2CH_2	KI	0.15	15	83

[a] DCB = $NaNH_2$ (2 equiv.)–Bu^tONa (1 equiv.)–KX (0.15–1.5 equiv.) prepared in THF at 45 °C. [b] The BRP corresponds to the duration between the first and ultimate red coloration during the condensation of 1 equiv. of $PhCH_2Cl$ (see ref. 4). [c] Isolated yield of $Ph_nCH_{3-n}CH_2Ph$.

for 1 h before use. The results obtained are reported in Table 1.† The efficiencies of the DCBs as evaluated from their basic regeneration power (BRP).[4] From these data it clearly appears that the simple addition of a potassium salt to a Na^+ containing CB strongly improves its efficiency. Of course with KBr and KI, part of the BRP increase could be due to halogen exchange with $PhCH_2Cl$. However, control experiments showed, as expected under the experimental conditions used, that such exchanges did not play an important part. BRP improvement depends on the amount of the added salt. Such an observation was not unexpected since the nature of the aggregates and hence their reactivity depends on the ratio of their constituents.[5] Such a phenomenum has been observed by Hall *et al.*[6] in mixed aggregation of lithium halides with lithium 2,2,6,6-tetramethylpiperidide.

The above observations are not limited to kinetic effects. Indeed carbonation of Ph_3C^- prepared from CB led to 40% of the corresponding acid while DCB led to 55%. From our previous work[4] we conclude that such a difference is significant and reflects a basicity increase.

In conclusion, these experiments add further support to aggregative activation principles. An extension of these first results as well as their applications will be published in the future.

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† Note that the slightly lower yields observed in entries 12–17 are due to the increase of the basicity of the reagent and the concomitant formation of *trans*-stilbene from the benzyl halide.

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