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tion was then initiated by adding **1b**. Aliquots were removed and immediately made weakly acid by the addition of an appropriate amount of 0.1 N aqueous perchloric acid. (A control experiment had shown that in weakly acid solution the rate of exchange of *i*-Pr*SH with **1b** is negligible.) The isolation of the thiol as its silver salt and the determination of its level of activity was done in the same manner as described for 2-methyl-2-propanethiol.

Kinetic Study of Other Reactions of 1. Unlike some of the reactions of thiolate ions with **1**, none of the reactions of **1** with cyanide ion showed biphasic behavior when studied in HCN–CN⁻ buffers containing a large stoichiometric excess of cyanide ion over **1**. The reactions were also slow enough that they could be followed by conventional spectrophotometry. A measured volume (3.5 mL) of a 60% dioxane solution containing the desired concentrations of CN⁻ and HCN was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a spectrophotometer. The reaction was then initiated by adding 35 μL of a 0.05 M solution of **1** in pure dioxane and followed by monitoring the decrease

in absorbance at an appropriate wavelength (275 nm for **1a** and **1b**, 280 nm for **1c**). The reaction of sulfite ion with **1a** was followed in a similar manner with a 1:1 Na_2SO_3–$NaHSO_3$ buffer.

The disappearance of **1a** in piperidine buffers was followed at 250 nm. It exhibited biphasic behavior, an initial rather rapid increase in absorbance, followed by a much slower decrease. The rates of the two processes were sufficiently different that one could easily determine accurately the absorbance at the end of the first stage of the reaction.

Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 18.[1] Study of the Nature of Complex Reducing Agents Prepared from Nickel and Zinc Salts

Jean-Jacques Brunet,[2a] **Denis Besozzi,**[2a] **Alain Courtois,**[2b] **and Paul Caubere**[*2a]

Contribution from the Laboratoire de Chimie Organique I, Université de Nancy I, Faculté des Sciences, B.P. 239, 54506 Vandoeuvre les Nancy, France. Received April 1, 1982

Abstract: Complex reducing agents "NaH–RONa–MX$_n$" (referred to as MCRA) are new versatile reagents that have already found many applications in organic synthesis. In the present study, the composition and structure of NiCRA and ZnCRA (CRA prepared from a nickel salt and a zinc salt, respectively) have been investigated. It has been found that, in both reagents, the metal (Ni or Zn) is formally in a zero-valent oxidation state. The active part of NiCRA is constituted of new species (formed from Ni⁰ (1 equiv), RONa (R = *t*-Bu) (2 equiv), NaH (2 equiv), and maybe some AcONa) in which each constituent has lost its own characteristics. A picture of the structure of these new species is proposed. The composition of the active part of ZnCRA is less clear. Indeed, associations between RONa (R = *t*-Am) and Zn⁰ have been evidenced, but these species do not exhibit the reducing properties of ZnCRA, e.g., toward carbonyl compounds. In fact, control experiments have shown that no ketone reduction occurred in the absence of NaH. These observations led us to propose that the active part of ZnCRA should be constituted of associations of the type $[(t\text{-}AmO)_yH_zZnNa_{y+z}]_n$, which may be formed, in low concentration, from NaH and the inactive species $[(t\text{-}AmO)_xZnNa_x]_n$.

Over the past few years, we have been interested in a new kind of reducing system, the complex reducing agents[3] (abbreviated CRA[4]). These reagents, formulated as "NaH–RONa–MX$_n$", are very easily prepared from sodium hydride, a metal salt,[4] and an alcohol (generally a tertiary alcohol). They resulted from the concept of activation by alkoxides, which was reported earlier from this laboratory concerning complex bases "NaNH₂–RONa".[5]

Until now, we have essentially explored the possible synthetic applications of CRA. It has been shown that they are very useful reagents in the field of chemical reductions[6] and that they allow many highly selective reductions.[6c,7] They also constitute a new

source of heterogeneous, very active and selective hydrogenation catalysts such as Nic.[8] Their preparation concept has been applied to the development of new coupling reagents[9] and to the development of reaction media,[10] allowing unprecedented cobalt- and iron-catalyzed carbonylations of organic halides under atmospheric carbon monoxide pressure.[11,12] Finally, from intensive work now in progress in this laboratory, it can be affirmed that other applications of CRA are still very promising.

The usefulness of CRA having been proved, it was decided to undertake a study with the object of obtaining better knowledge about the nature of the active species involved in these surprising reagents. However, it is a very hard task to determine the constitution and reaction pathways of CRA—heterogeneous

(1) Part 17: Brunet, J. J.; Besozzi, D.; Caubere P. *Synthesis* **1982**, 721.

(2) (a) Laboratoire de Chimie Organique I, NANCY, ERA CNRS no. 476. (b) Laboratoire de Minéralogie-Cristallographie, NANCY, ERA CNRS no. 162.

(3) (a) Gillaumet, G.; Mordenti, L.; Caubere, P. *J. Organomet. Chem.* **1975**, *92*, 43. (b) Guillaumet, G.; Mordenti, L.; Caubere, P. *Ibid.* **1975**, *102*, 353. (c) Caubere, P. *Top. Curr. Chem.* **1978**, *73*, 50 and references cited therein.

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(5) Caubere, P. *Acc. Chem. Res.* **1974**, 301 and references cited therein.

(6) (a) Brunet, J. J.; Mordenti, L.; Loubinoux, B.; Caubere, P. *Tetrahedron Lett.* **1977**, 1069. (b) Brunet, J. J.; Mordenti, L.; Caubere, P. *J. Org. Chem.* **1978**, *43*, 4804. (c) Vanderesse, R.; Brunet, J. J.; Caubere, P. *Ibid.* **1981**, *46*, 1270.

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(8) Brunet, J. J.; Gallois, P.; Caubere, P. *Tetrahedron Lett.* **1977**, 3955. Brunet, J. J.; Gallois, P.; Caubere, P. *J. Org. Chem.* **1980**, *45*, 1937. Gallois, P.; Brunet, J. J.; Caubere, P. *Ibid.* **1980**, *45*, 1946.

(9) Loubinoux, B.; Vanderesse, R.; Caubere, P. *Tetrahedron Lett.* **1977**, 3951. Vanderesse, R.; Brunet, J. J.; Caubere, P., results to be published.

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(11) Brunet, J. J.; Sidot, C.; Loubinoux, B.; Caubere, P. *J. Org. Chem.* **1979**, *44*, 2199.

(12) Brunet, J. J.; Sidot, C.; Caubere, P. *J. Org. Chem.* **1981**, *46*, 3147.

Activation of Reducing Agents

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Table I. Hydrogen Evolution during the Preparation of NiCRA and Related Control Experiments[a]

reagents involved (mmol)	hydrogen evolution, mmol	
	expctd	obsd
NaH (60)	0	0
NaH (60) + *t*-BuOH (20)	20	20
t-BuONa[b] (20)	0	0
t-BuONa[b] (20) + Ni(OAc)₂ (10)	0	0
NaH (60) + Ni(OAc)₂ (10)	?	1–2
NaH (60) + Ni(OAc)₂ (10) + *t*-BuOH (20)	?	30

[a] The reagents were put (or mixed) in 30 mL of DME at 63 °C, and the reaction mixture was stirred for 2 h at 63 °C (see Experimental Section). [b] Limpid solutions of *t*-BuONa in DME (no OH stretching vibration in the IR spectrum) were obtained by reacting *t*-BuOH (20 mmol) with excess sodium wire at 63 °C overnight and then removing the remaining sodium wire.

reagents—the *insoluble part of which appears, at first sight, to be an amorphous material. Indeed, it was not possible to obtain monocrystals whose structure could have been used to deduce the structure of active species. Thus, it was decided to turn toward experiments likely to furnish the more accurate information about these reagents.

In the present paper, we report our results concerning the nature of the species involved in NiCRA and ZnCRA (CRA prepared from a nickel and a zinc salt, respectively), the two reagents of which the reactivity toward organic substrates has been the most studied in this laboratory.

Results

Study of NiCRA. We chose to study the NiCRA NaH–*t*-BuONa–Ni(OAc)₂ (40–20–10 mmol). This reagent was prepared as previously described[4] by adding *t*-BuOH (20 mmol) to a preheated (63 °C) suspension of NaH (60 mmol) and Ni(OAc)₂ (10 mmol) in 1,2-dimethoxyethane (DME) (see Experimental Section). During the preparation (2 h at 63 °C), we observed, as expected, a gas evolution. If this gas originated from the ordinary reaction of *t*-BuOH with NaH, a 20-mmol gas evolution might be expected. In fact, a 30-mmol gas evolution was measured; i.e., a 10-mmol excess was observed. That all the gas evolved was hydrogen was easily demonstrated by using it to perform near quantitative catalytic hydrogenation of 30 mmol of an unsaturated substrate over Nic[8] (see Experimental Section).

Control experiments performed under simulated reaction conditions (DME, 63 °C) clearly showed that none of the reagents (NaH, *t*-BuONa and Ni(OAc)₂) taken alone or as couples (NaH–*t*-BuONa, NaH–Ni(OAc)₂, and *t*-BuONa–Ni(OAc)₂) led to such an excess gas evolution (Table I). (At most, a slight hydrogen evolution (1–2 mmol) was observed when Ni(OAc)₂ (10 mmol) was treated with NaH (60 mmol) in DME. It has also been verified that reaction of *t*-BuOH (20 mmol) with NaH (60 mmol) led to only 20 mmol of hydrogen evolution after 2 h at 63 °C in DME. Thus, any reaction of these reagents with the solvent could be discarded, and it was concluded that a 10-mmol hydrogen excess was formed during the preparation of NiCRA (1 mol H₂ per Ni[II] equivalent).

The reagents obtained after 30 mmol of hydrogen had evolved were submitted to hydrolysis in order to determine whether the hydrogen excess originated from NaH, and the volume of hydrogen thus evolved was measured. This volume (20 mmol) accounted for the amount of active hydride remaining in the reagent. Thus it was clear that 20 mmol of active hydride had been consumed during the preparation of NiCRA. These observations led to the conclusion that during the preparation of NiCRA, two hydride ions might react with one Ni[II], leading to hydrogen and Ni[0]:

$$2H^- + Ni^{II} \rightarrow Ni^0 + H_2 \qquad (1)$$
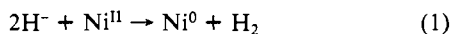
We then turned toward another important parameter, which is the localization of the main constituents of NiCRA. Indeed, NiCRA is a heterogeneous medium constituted (after decantation)

of a limpid liquid and of a black insoluble material. Centrifugation (see Experimental Section) of NiCRA under an inert atmosphere allowed full separation of these two phases.

As concerns the liquid phase, atomic absorption titration (see Experimental Section) indicated the total absence of nickel species. Hydrolysis, followed by GLC analysis with an internal standard, led to the conclusion that only traces (0.1–0.3 mmol) of *t*-BuONa were present in the liquid phase. (It has been verified that *t*-BuONa is completely soluble in DME at the same concentration as that used for the preparation of NiCRA). One possible explanation might have been found in the formation of cross aggregates between NaH and *t*-BuONa,[3c,5] thus inducing a lowering of the apparent solubility of *t*-BuONa. In fact, such was not the case. Centrifugation of a NaH–*t*-BuONa mixture (20–20 mmol) (prepared by reacting NaH (40 mmol) with *t*-BuOH (20 mmol) in DME), followed by hydrolysis of the liquid phase, indicated that a large part of the alkoxide was soluble in the liquid phase. All these experiments led to the conclusion that unless the alkoxide was destroyed during the preparation of NiCRA (such was not the case, vide infra), the nickel insoluble species held it in the solid material. Finally, these observations are in agreement with the finding that the liquid phase exhibited no reducing properties.

All the above data were confirmed by the analysis of the solid material obtained after centrifugation of NiCRA. As expected, atomic absorption titration indicated that all the starting nickel was included in the solid. Furthermore, hydrolysis of this material, followed by GLC analysis with an internal standard, led to the recovery of 99% of the *t*-BuOH, thus proving that no destruction of the activating agent had occurred and that all the *t*-BuONa was included in the solid phase. Finally, replaced in DME, this solid material led to a reagent that exhibited the usual reducing properties of NiCRA.

At this point of our work it seemed impossible to gain further information. So it was decided to study the X-ray powder patterns of the solid part of NiCRA. This technique had been used with success by Ashby and Watkins[13] during their work on the synthesis of metal hydrides. We felt that the methodology used by these authors would apply well to the problem of NiCRA.

Thus, after removal of the solvent from the NiCRA under vacuum, the X-ray powder pattern of the remaining solid material was recorded (Table II) (see Experimental Section).

Data concerning X-ray powder patterns of NaH, AcONa, and metallic nickel were available from the JCPDS powder diffraction file. For comparison, the X-ray powder patterns of solid *t*-BuONa (prepared in the same way as NiCRA, i.e., from a DME solution; see footnote b, Table I) and of the solid material obtained by reacting Ni(OAc)₂ (1 equiv) with *t*-BuONa (2 equiv) (see Experimental Section) were recorded. However, this latter material was found to be poorly crystallized, and only a few reflexions were observable. Finally, anhydrous Ni(OAc)₂ used for the preparation of NiCRA was found to be not crystallized.

Comparison of these data (Table II) led to some interesting conclusions. First, only traces of nickel metal were detectable from NiCRA. Secondly, none of the diffraction line groups expected for NaH and *t*-BuONa were observable in the NiCRA diagram (absence of the diffraction lines at *d* = 1.73 Å (s) and 1.47 Å (s) expected for NaH and of the lines at *d* = 9.62 Å (s), 6.61 Å (mw), 5.56 Å (mw), 5.11 Å (m), and 4.82 Å (m) expected for *t*-BuONa). Note that it has been verified that the amount of residual DME was about the same in solid *t*-BuONa (molar ratio DME/*t*-BuONa = 0.02) and in the solid material from NiCRA (molar ratio DME/*t*-BuONa = 0.03) and, in any case, quite negligible for X-ray diffraction patterns. On the contrary, some AcONa appeared present as such, although we could not determine the exact amount. Furthermore, the presence of some amount of the material obtained from a 2/1 reaction of *t*-BuONa with Ni(OAc)₂ was dismissed by the total absence of the diffraction line at *d* = 9.5 Å. Finally, unattributed diffraction lines were observed in the NiCRA diagram, some of which were of high

(13) (a) Watkins, J. J.; Ashby, E. C. *Inorg. Chem.* 1974, *13*, 2350 and references cited therein. (b) Ashby, E. C.; Watkins, J. J. *Ibid.* 1973, *12*, 2493.

Table II. X-ray Powder Patterns of the Solid Material from NiCRA and Related Possible Components[b]

NiCRA[a]		NaH[c]		t-BuONa[a]		AcONa (α)[c]		AcONa (β)[c]		Ni metal[c]		solid from 2/1 reactn of t-BuONa with Ni(OAc)$_2$[d]	
d, Å	I/I$_1$	d, Å	I/I$_1$	d, Å	I/I$_1$	d, Å	I/I$_1$	d, Å	I/I$_1$	d, Å	I/I$_1$	d, Å	I/I$_1$
10.04	s	2.83	s	11.62	w	10.1	s	9.95	vvs	2.03	s	9.5	vs
9.18	s	2.44	s	9.62	s	3.87	s	4.97	w	1.76	m	4.64	s
5.86	vw	1.73	s	9.11	vs	2.98	s	4.61	mw	1.24	mw	3.63	w
5.62	vw	1.47	s	6.61	mw	2.95	m	3.60	w	1.06	mw	3.27	w
5.06	mw	1.41	m	6.06	w	2.86	w	3.31	w	1.02	w	2.88	m
4.95	mw	1.22	w	5.77	w	2.64	w	3.275	m			2.56	w
4.61	mw	1.12	m	5.56	mw	2.09	mw	2.887	m			2.04	w
4.26	mw	1.09	m	5.11	m	2.05	w	2.77	w			1.91	w
3.90	w	0.996	m	4.82	m	1.76	w	2.49	w				
3.58	mw	0.939	m	4.59	mw								
3.26	mw			4.40	mw								
3.03	w			4.28	mw								
2.88	m			4.09	mw								
2.80	m			3.61	w								
2.76	mw			3.02	mw								
2.48	w												
2.43	vw												
2.19	w												
2.13	mw												
2.03	w												

[a] Recorded in impervious cells with beryllium windows (see Experimental Section). The lines for beryllium have been discarded. For t-BuONa preparation, see footnote b, Table I.   [b] Key: w, weak; m, medium; s, strong; v, very.   [c] From JCPDS powder diffraction file. [d] See Experimental Section.

intensity (d = 10.04 Å, superimposed with one line from AcONa, and d = 9.18 Å).

These results allow us to conclude that at least part of the NiCRA (if not all) was in a crystalline form. Furthermore, NiCRA appears to be constituted of new species in which each constituent (or precursor) has lost its own characteristics to participate in the formation of new structures.

Before discussing these structures, we shall report the results obtained during the study of ZnCRA.

Study of ZnCRA. The same kind of study has been performed with a ZnCRA. We chose the system NaH–t-AmONa–ZnCl$_2$ (40–10–10 mmol) whose applications had been developed in selective reductions.[7b]

This reagent was prepared as usual[7b] by adding t-AmOH (10 mmol) to a suspension of NaH (50 mmol) and ZnCl$_2$ (10 mmol) in refluxing THF (see Experimental Section). After 2 h of stirring under a nitrogen atmosphere, the reagent (heterogeneous) was ready for use.

Thus, the preparation of ZnCRA involved heating a NaH–ZnCl$_2$ mixture from room temperature to 63 °C before adding the activating alcohol. The reaction of NaH with ZnCl$_2$ (in 1/1 molar ratio) had been studied by Watkins and Ashby,[13a] who reported this reaction to proceed (room temperature, 1 day) according to

$$NaH + ZnCl_2 \rightarrow 0.5ZnCl_2 + NaCl + 0.5ZnH_2$$
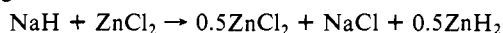
However, the X-ray powder pattern obtained for the solid part of this reaction medium did not exhibited the classical lines for ZnH$_2$,[13] and these authors concluded that the ZnH$_2$ had been destroyed in an unknown manner to produce Zn metal.

Taking these results into account, it was decided to study the reaction of NaH (50 mmol) with ZnCl$_2$ (10 mmol) in refluxing THF, i.e., under the conditions used for the preparation of ZnCRA. The salient features of this study are worth noting. First, NaH readily reacted with ZnCl$_2$ (see Experimental Section) to produce 10 mmol of evolved hydrogen and, secondly, the X-ray powder pattern of the solid material (obtained after removing the solvent under reduced pressure) contained only the lines for NaCl, NaH excess, and zinc metal. Furthermore, hydrolysis of this material indicated that it contained 30 mmol of unreacted NaH. Thus, it must be concluded that during ZnCRA preparation, the first reaction to take place was reduction of ZnCl$_2$ by NaH:

$$2NaH + ZnCl_2 \rightarrow 2NaCl + H_2 + Zn \text{ metal}$$

Accordingly, considering the ZnCRA preparation procedure, it was clear that the zinc salt had been reduced before t-AmOH was added. Further hydrogen evolution induced by addition of t-AmOH (10 mmol) to the reaction mixture was measured and found to reach 10 mmol.

Finally, hydrolysis of ZnCRA at the end of its preparation led to 20 mmol of hydrogen evolution, thus confirming the above observations. Note that the above data discarded the possible reaction of t-AmOH with a very reactive form of zinc metal:

$$Zn + 2t\text{-AmOH} \rightarrow Zn(O\text{-}t\text{-Am})_2 + H_2$$
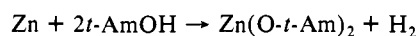
Indeed, if such a reaction had occurred (i) only 5 mmol of hydrogen gas evolution would have been recorded and (ii) no NaH consumption would have been observed.

Continuing our study of ZnCRA, we then determined in which phase were located the main constituents. Centrifugation of ZnCRA under inert atmosphere allowed full separation of the two phases, which were analyzed separately.

The clear liquid phase was shown to contain no zinc species (dithizone titration[14]). Hydrolysis of this phase followed by GLC analysis with an internal standard indicated the presence of 3.6–4 mmol of t-AmOH. Finally, as might be expected, this phase exhibited no reducing properties.

Analysis of the solid phase confirmed that all the zinc was located in the insoluble part of ZnCRA. Hydrolysis of this material followed by GLC analysis with an internal standard led to the recovery of 6–6.4 mmol of t-AmOH, thus indicating that no destruction of t-AmOH had occurred during the preparation of ZnCRA.

Finally, an important question remained to be answered. Indeed, we have shown that NaH did reduce ZnCl$_2$ before addition of the activating alcohol. Thus, it was very important to determine whether the zinc metal remained as such in the solid part of ZnCRA or whether it had been included in a new species, just as Ni^0 in NiCRA. Study of the X-ray powder pattern of the solid part of ZnCRA obtained after removing the solvent under vacuum answered this question (Table III, see Experimental Section).

The X-ray powder patterns of ZnCl$_2$, Zn metal, NaCl, and NaH are described in the JCPDS powder diffraction file. For comparison, the X-Ray powder patterns of t-AmONa and of the

(14) Charlot, G. "Chimie Analytique Quantitative"; Masson: Paris, 1974; Vol. II, 565.

Table III. X-ray Powder Patterns of the Solid Material from ZnCRA and Related Possible Components[h]

ZnCRA[a,b]		NaH[c]		t-AmONa[d]		Zn metal[c]		ZnH₂[e]		solid from 5/1 reactn of NaH with ZnCl₂[f,g]		solid from 1/1 reactn of t-AmONa with ZnCl₂[a,f]		NaCl[c]	
d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁	d, Å	I/I₁
10.48	mw	2.83	s	10.53	m	2.473	m	4.90	w	3.241	vw	12.80	w	3.22	w
9.89	w	2.44	s	6.58	w	2.308	m	3.79	w	2.811	s	8.85	m	2.80	s
3.26	w	1.73	s	5.79	w	2.091	s	2.82	s	2.761	vw	7.62	w	1.98	s
2.819	s	1.47	s	5.15	m	1.687	m	2.60	s	2.467	mw	7.28	mw	1.72	w
2.469	w	1.41	m	4.84	mw	1.342	m	2.46	s	2.432	mw	6.75	w	1.62	m
2.432	m	1.22	mw	4.41	mw	1.332	m	2.29	m	2.30	mw	5.55	w	1.40	w
2.31	vw	1.12	m	4.24	mw	1.237	w	2.08	s	2.088	m	4.51	mw	1.256	mw
2.087	mw	1.09	m	4.03	w	1.173	m	1.90	ms	1.990	m	2.811	m		
1.974	s	0.996	m	3.84	w	1.154	w	1.68	m	1.720	w	1.969	Be		
1.969	Be	0.939	m	3.45	w	1.124	w	1.62	ms	1.681	w	1.786	mw		
1.790	w			2.96	w	1.091	w	1.475	s	1.623	w	1.723	Be		
1.728	Be			2.735	w	1.046	w	1.37	ms	1.469	w	1.624	mw		
1.68	w			2.62	w			1.335	m	1.406	w				
1.623	mw			2.405	w			1.329	m	1.338	w				
1.465	m			2.170	w			1.30	w	1.330	w				
1.403	mw			2.105	w			1.234	w	1.259	w				
1.324	mw			1.972	Be			1.169	m	1.171	w				
1.255	mw			1.791	w			1.15	w	1.150	w				
1.137	m			1.726	Be			1.119	m						
								1.09	m						

[a] Recorded in impervious cells with beryllium windows. [b] The diffraction line groups of all ZnCl₂ forms (α or β) and of ZnCl₂ obtained by stripping a THF solution of ZnCl₂ to dryness[13a] were absent from this diagram. [c] From JCPDS powder diffraction file. [d] Prepared from t-AmOH and Na, as was t-BuONa, see footnote b, Table I, and Experimental Section. [e] From ref 13a. [f] See Experimental Section. [g] Recorded in Lindemann tube, see Experimental Section. [h] Key: w, weak; m, medium; s, strong; v, very.

solid material obtained by reacting t-AmONa (10 mmol) with ZnCl₂ (10 mmol) (see Experimental Section) were recorded (Table III), although the presence of the latter species in ZnCRA was highly unlikely (vide supra).

The salient point of this study is that, contrary to what was found for NiCRA, the X-ray powder pattern of ZnCRA exhibited the characteristic diffraction lines for NaH and zinc metal. It also exhibited the lines for NaCl and some new, unattributed, medium to weak intensity lines (d = 10.48, 9.89, and 1.79 Å). Approximate evaluation (see Experimental Section) of the amount of each constituent showed that most of the NaH was present as such and that about 30% of the total zinc was present as zinc metal. Nevertheless, 70% of the zinc and all the alkoxide were included in new species, as shown by the absence of the diffraction lines for t-AmONa and by the presence of new unattributed lines. Interestingly, these results also indicate that the 3.6–4 mmol of t-AmONa that was soluble in the liquid phase (vide supra) had been included in these new species during removal of the solvent under reduced pressure.

The main conclusion of the above study is that ZnCRA is not a trivial mixture of NaH, t-AmONa, and zinc metal. In other words, it appears that generation of t-AmONa in the presence of zinc metal (under a very reactive form as indicated by investigations currently in progress in this laboratory) formed by reduction of ZnCl₂ by NaH led to dissociation of zinc crystals to give new species where Zn⁰ is associated with t-AmONa!

Discussion

It clearly appears from the above studies that both NiCRA and ZnCRA are constituted of new species in which the metal (Ni or Zn) is formally in a zero-valent oxidation state. These findings are consistent with some previously reported properties of CRA. For instance, NiCRA is a very efficient heterogeneous hydrogenation catalyst (referred to as Nic).[8] Moreover, when this reagent is prepared in the presence of ligands such as phosphines or 2,2'-bipyridine, it loses its reducing properties and behaves as a coupling reagent.[9] Likewise, prepared in the presence of 1,3-butadiene, NiCRA behaves as an oligomerization catalyst.[9] The properties of the nickel derivatives thus obtained are generally characteristic of Ni⁰ complexes.[15] However, the present study affords further interesting information. We shall first comment on NiCRA.

(15) See, for example: Jolly, P. W.; Wilke, G. "Organic Chemistry of Nickel"; Academic Press: New York, 1974 (Vol. I), 1975 (Vol. II).
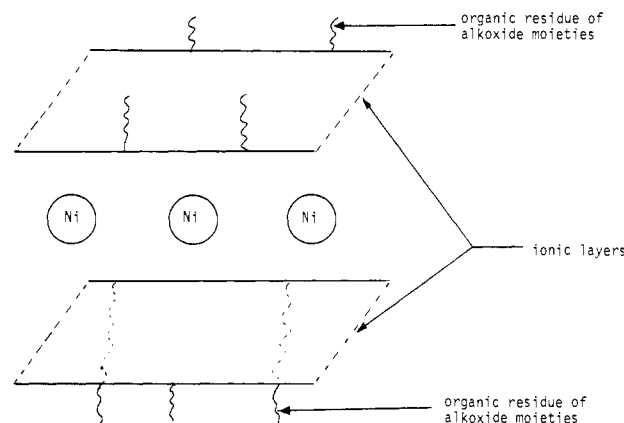
Figure 1.

From the present data, NiCRA appears to be constituted of aggregates induced by association of patterns containing nickel atoms surrounded by ionic moieties Na⁺, H⁻, t-BuO⁻, and maybe some AcO⁻.

It is well-known that alkali metal alkoxides as well as alkali metal ketone enolates are associated in aggregates.[16,17] When isolation of crystalline samples has been possible, X-ray diffraction studies have shown these materials to be associated as tetramers or hexamers.[16,17] Under polymer form, association of such patterns may occur, leading to a somewhat regular distribution of atoms.

The same kind of association may be expected in complex bases NaNH₂–RONa[5] as well as in activated sodium hydride NaH–RONa.[3c] Indeed, it is well-known that alkali metal alkoxides as well as alkali metal ketone enolates associate with alkali metal amides to give new aggregates (complex bases) possessing their own properties.[3c,5] Extension of this concept has led to the activation of the reducing power of NaH when associated with sodium alkoxides.[3c]

So, the active part of NiCRA may be viewed as constituted of nickel atoms included in a polymer matrix made up of NaH, t-BuONa, and maybe some AcONa. In other words, nickel atoms

(16) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: New York, 1978, and references cited therein.

(17) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2617; Seebach, D.; Anstutz, R.; Dunitz. J. D. *Ibid.* **1981**, *64*, 2622.

should be located in cavities constituted of Na$^+$, H$^-$, *t*-BuO$^-$ (and AcO$^-$). These hypotheses led us to tentatively propose the general picture of Figure 1. NiCRA should involve some sandwich ionic layers inside which the nickel atoms should be maintained. Some cohesion between layers could be assumed by positive interactions between the organic residue of the alkoxide moieties. Of course, in the reaction conditions the solvent may play a role in such structures, particularly as regards these interactions between different layers.

Such a picture implies a rather regular distribution of nickel atoms. As nickel is the most X-ray-diffusing atom in NiCRA, this regular distribution should be manifested by strong diffraction lines in the X-ray powder pattern. The presence of strong, unattributed diffraction lines (vide supra) in the X-ray powder pattern from NiCRA seems to be consistent with this expectation.

Consequently, the unusual reducing properties of NiCRA could be interpreted by assuming that during reductions of organic substrates, nickel centers anchor the substrate and assure the electronic transfer from the electron reservoir constituted by the ionic layers.

With regards to ZnCRA, the situation can appear to be simpler at first sight. In fact, it is much more complicated.

Indeed, it appears from the present study that the new species in ZnCRA result from an association of *t*-AmONa with Zn^0, which could be written as $[(t\text{-AmO})_x\text{ZnNa}_x]_n$. This formulation agrees with the fact that most of the NaH has been found as such in the study of the X-ray powder pattern from ZnCRA. However, the reasons that these species exhibit high reducing properties were far from obvious! Nevertheless, the ZnCRA presently studied is particularly efficient for the reduction of carbonyl groups in both saturated and α,β-unsaturated ketones.[6b,7b] So, we carried out some control experiments.

During these experiments, we have first shown that zinc metal produced by reacting ZnCl$_2$ (10 mmol) with NaH (20 mmol) in THF (vide supra) exhibited no reducing properties toward ketones. Thus, the possibility of reduction by Zn of the ketones to radical anions followed by H atom abstraction from the solvent must be discarded. Note that although NaH has been shown to reduce nonenolizable ketones under certain conditions,[18] this reagent is unable to reduce enolizable ketones under the conditions used in this work.[6b] In the same way, we have previously shown that NaH–RONa is a better reducing agent than NaH alone,[3c] but inefficient too for the reduction of enolizable ketones.[6b]

It was also found that the reagent obtained (just like ZnCRA, but without NaH excess) by adding *t*-AmOH (10 mmol) to a mixture of ZnCl$_2$ (10 mmol) and NaH (30 mmol) in refluxing THF exhibited no reducing properties toward ketones either. This experiment demonstrated that the species formulated above as $[(t\text{-AmO})_x\text{ZnNa}_x]_n$ had no reducing properties. On the contrary, the reagent obtained from NaH (50 mmol) and ZnCl$_2$ (10 mmol) (in other words, NaH–Zn metal–NaCl, vide supra) was able to reduce ketones! However, its efficiency was generally much lower than that of ZnCRA. It might be thought that in the latter reagent, excess NaH reduced a small fraction of the ketone, thus generating an alkoxide leading to a new, more or less efficient, ZnCRA.

All these observations clearly indicated that no reduction occurred in the absence of NaH and zinc derivatives. Consequently, we very tentatively proposed that, in fact, the active part of ZnCRA is constituted of species in which NaH is associated with zinc centers, just as for NiCRA (vide supra). So, ZnCRA may be viewed as a mixture of NaH, $[(t\text{-AmO})_x\text{Zn}(\text{Na})_x]_n$, and $[(t\text{-AmO})_y(\text{H})_z\text{Zn}(\text{Na})_{y+z}]_n$. With such reagents, reductions should take place on the active parts, which could be regenerated from NaH and the remaining inactive zinc centers $[(t\text{-AmO})_x\text{Zn}(\text{Na})_x]_n$.

Experimental Section

Materials. Sodium hydride was obtained either from Fluka (55–60% in oil) or from Degussa (60% in oil). Titration of each batch before use was carried out by classical techniques.[18] For each run, NaH was washed

several times in the reaction flask with the solvent (DME or THF) under nitrogen. DME (Fluka) was distilled from sodium under nitrogen and stored over sodium wire. Badische Anilin, reagent-grade THF, was distilled from benzophenone–sodium couple prior to use. For both solvents, the absence of peroxides was checked before each run. *tert*-Butyl and *tert*-amyl alcohols were distilled from sodium. Nickel acetate (Prolabo) and zinc chloride (Fluka) were dried in vacuo for 12–14 h at 100–120 °C. All reactions were carried out under nitrogen R (L'Air Liquide).

General Procedures. GLC analyses were performed on either a Carlo-Erba GI 452 or a Girdel 3000 apparatus (flame ionization) equipped with 5-m 15% Carbowax 20 M columns. Atomic absorption titrations of nickel were carried out on a Varian Techtron photometer (Model 1200) at 352.4 nm. Titrations of zinc were carried out by the method of extraction with dithizone[14] (accuracy 1%). Centrifugations were performed with a Janetski apparatus (Model T 32) at about 900g. IR spectra were recorded with a Perkin-Elmer spectrophotometer (Model 580 B). X-ray powder data were obtained on a C.G.R. diffractometer (equipped with a vertical-axis-type goniometer) with quartz filtered Cu Kα radiation (transmission mode).

Preparation of NiCRA. *t*-BuOH (20 mmol), diluted in 10 mL of THF, was added dropwise (through a funnel of the pressure-equalizing type) to a preheated (63 °C), vigorously stirred suspension of NaH (60 mmol) and Ni(OAc)$_2$ (10 mmol) in 20 mL of DME under a slow stream of nitrogen. After 2 h of stirring (magnetically) at this temperature, NiCRA was ready to use in carrying out reductions.

Hydrogen Evolution during the Preparation of NiCRA (Table I). The suspension of NaH and Ni(OAc)$_2$ in DME was heated to 63 °C under nitrogen. Then, the nitrogen stream was suppressed, and the reflux condenser was connected (through a drying column filled with CaCl$_2$) to a classical gas buret with a leveling bulb. Then *t*-BuOH, diluted as above, was added dropwise and the volume of hydrogen evolved measured on the graduated buret after 2 h of stirring at 63 °C.

Hydrogen Evolutions during Control Experiments (Table I). The same procedure as described above was used. The reagent(s) were added to DME at 63 °C, either as solids (NaH, Ni(OAc)$_2$) via a wide bent test tube[19] or as solutions in DME (*t*-BuOH or *t*-BuONa) through the funnel described above. Hydrogen evolutions were measured as described above after 2 h of stirring at 63 °C.

Hydrogen Identification (Table I). The gas evolved from the above experiments was kept in the buret and used to perform catalytic hydrogenation of 1-octene over Nic.[8] For instance, the gas evolved from NiCRA preparation (30 mmol) was shown to allow hydrogenation of 30 mmol of 1-octene (EtOH as solvent, Ni amount: 0.5 mmol) to yield 28.5 mmol of octane and 1.5 mmol of unreacted 1-octene (GLC analysis with internal standard).

Hydrogen Evolution during Hydrolysis of NiCRA. Excess water was added dropwise to the reaction medium at 63 °C through the funnel (pressure-equalizing type) and the hydrogen evolution (see text) measured as described above.

Localization of the Constituents of NiCRA. At the end of the preparation of NiCRA, the reaction medium was allowed to cool to room temperature, syringed, and placed under argon in tubes, stoppered with septum caps, for centrifugation. The mixture was centrifuged at 900g for 1 h. The limpid phase was syringed (while admitting argon through another syringe), and DME was added to the remaining solid. The tube was then shaken and centrifuged again. This procedure was repeated three times and thus allowed full separation of the two phases.

Analysis of the Liquid Phase. This phase was hydrolyzed, acidified, and extracted with diethyl ether. The ether extracts were dried over MgSO$_4$. GLC analysis (with cyclooctane as internal standard) indicated the presence of 0.1–0.3 mmol of *t*-BuOH. The organic phase was then evaporated to dryness and added to the aqueous phase of the previous extraction. The material was then treated with dilute nitric acid for several hours and submitted to atomic absorption analysis (352.4 nm). No nickel traces could be detected.

Analysis of the Solid Phase. The solid phase was carefully hydrolyzed, acidified, and extracted with diethyl ether. The ether extracts were dried over MgSO$_4$. GLC analysis, as described above, indicated the presence of 9.7–9.9 mmol of *t*-BuOH. This organic phase was then evaporated to dryness, and the residue was added to the aqueous phase obtained above, which was then treated with dilute nitric acid. Atomic absorption titration (352.4 nm) indicated the presence of 10 mmol of nickel.

X-ray Powder Analysis of NiCRA and Related Possible Components (Table II). At the end of the preparation of NiCRA, the reaction medium was allowed to cool to room temperature, and the solvent was then removed by heating to 40 °C under reduced pressure for 4 h (a slow stream of argon was maintained throughout this operation). The stop-

(18) Caubere, P.; Moreau, J. *Bull. Soc. Chim. Fr.* **1971**, 3276.

(19) Plesek, J.; Hermanek, S. "Sodium Hydride"; Iliffe: London, 1968.

pered reaction flask was then placed in a glove box (filled with argon) and the solid material finely ground in a mortar. Part of the resulting powder was then either sealed in a 0.5-mm Lindemann tube or put in an impervious cell with beryllium windows and then submitted to X-ray analysis.

X-ray powder patterns of *t*-BuONa (see footnote b, Table I) and of the solid material obtained by reacting *t*-BuONa (20 mmol) with Ni(O-Ac)$_2$ (10 mmol) were obtained by a similar procedure.

Preparation of ZnCRA. Gas Evolution. *t*-AmOH (10 mmol) diluted in 10 mL of THF was added dropwise through a funnel (of the pressure-equalizing type) to a preheated (reflux) suspension of NaH (50 mmol) and ZnCl$_2$ (10 mmol) in 20 mL of THF under a slow stream of nitrogen. After 2 h of stirring (magnetically) at 63 °C, the reagent was ready to use for reductions. The hydrogen evolution, measured on and after addition of *t*-AmOH, was found to reach 10 mmol (see text).

Reaction of NaH with ZnCl$_2$. ZnCl$_2$ (10 mmol) was added via a wide bent test tube to a suspension of NaH (50 mmol) in 30 mL of refluxing THF. The total hydrogen evolution (10 mmol) was measured, as described above, after 2 h at 63 °C. However, this hydrogen evolution reached 10 mmol within about 15 min. After removal of the solvent under reduced pressure, the remaining solid material was treated as described above for NiCRA, and the powder was submitted to X-ray diffraction analysis (see text and Table III).

Hydrolysis of ZnCRA. Hydrolysis of ZnCRA was achieved as described above for NiCRA.

Localization of the Main Constituents. After separation by centrifugation as for NiCRA, the two phases were analyzed. Titrations of *t*-AmOH after hydrolysis indicated that the liquid phase contained 3.6–4 mmol of *t*-AmONa and that 6–6.4 mmol of *t*-AmONa were included in the solid phase. Both phases were hydrolyzed and treated with dilute HCl. The zinc content of the corresponding aqueous phases was determined by extraction with dithizone[14] and titration. These titrations indicated that all the zinc (10 mmol) was located in the solid phase.

X-ray Powder Analysis of ZnCRA and Related Possible Components (Table III). The solid material, obtained after removing the solvent from ZnCRA, was treated as described above for NiCRA and the powder submitted to X-ray diffraction analysis (Table III). Estimation of zinc metal and NaH contents was obtained by assuming that all the NaCl was free both in ZnCRA and in the mixture NaH–Zn metal–NaCl (20–10–20 mmol) (obtained by reaction of 40 mmol of NaH with 10 mmol of ZnCl$_2$ as described above). NaCl was thus used as an internal standard, and we have compared the intensities of the line of Zn at $d = 2.09$ Å (i.e., the Zn$_x$ line) and of NaH at $d = 2.44$ Å (i.e., the NaH$_8$ line) to that of NaCl at $d = 1.98$ Å (i.e., the NaCl$_9$ line) in both diagrams. For ZnCRA, the Zn$_x$ line intensity was found to be 30% of that expected for 10 mmol and the NaH$_8$ line intensity about 100% of that expected for 20 mmol. *t*-AmONa was obtained by treating *t*-AmOH with excess sodium wire in refluxing THF. After 12 h of reaction, the excess sodium wire was discarded and the clear solution (no OH stretching vibration in the IR spectrum) evaporated to dryness. The resulting powder was then submitted to X-ray diffraction analysis.

The reaction of NaH (50 mmol) with ZnCl$_2$ (10 mmol) has been described above. Finally, the reaction of *t*-AmONa (10 mmol) with ZnCl$_2$ (10 mmol) was performed by adding ZnCl$_2$ to a solution of *t*-

AmONa in refluxing THF. After 2 h of stirring, the reaction medium was treated in the classical manner to afford a powder, which was submitted to X-ray diffraction analysis.

Control Experiments Concerning the Reactivity of ZnCRA toward Ketones. Reduction of Cyclohexanone with ZnCRA. Cyclohexanone (10 mmol) diluted in 10 mL of THF (together with 0.5 g of tridecane as internal standard) was added at 45 °C to ZnCRA, prepared as above. After 17 h of stirring at 45 °C, GLC analysis of small aliquots indicated 98% cyclohexanol formation.

Reduction of Cyclohexanone with Zinc Metal. Cyclohexanone (10 mmol) diluted in 10 mL of THF (together with 0.5 g of tridecane) was added at 45 °C to the mixture obtained by reacting NaH (20 mmol) with ZnCl$_2$ (10 mmol) (vide supra). After 17 h of stirring at 45 °C, GLC analysis of small aliquots indicated the presence of 100% recovered cyclohexanone.

Reduction of Cyclohexanone with [(*t*-AmO)$_x$ZnNa$_x$]. The reaction was performed as described above by reacting cyclohexanone with the reagent obtained, just as for ZnCRA, but using the following ratio of reagents: NaH (30 mmol), ZnCl$_2$ (10 mmol), *t*-AmOH (10 mmol). After 17 h of reaction at 45 °C, GLC analysis of small aliquots indicated 18% cyclohexanol formation and the presence of 82% recovered cyclohexanone.

Reduction of Cyclohexanone with NaH–ZnCl$_2$ (50–10 mmol). Cyclohexanone (10 mmol) was treated with the reagent obtained by reacting ZnCl$_2$ (10 mmol) with NaH (50 mmol) in THF as described above. After 17 h of reaction at 45 °C, GLC analysis of aliquots indicated 38% cyclohexanol formation and the presence of 60% recovered cyclohexanone.

Conclusion

This work has provided much basic information about the composition of NiCRA and ZnCRA and allowed us to propose a first picture for the structure of both reagents.

From the hypotheses formulated in this paper about the structures of CRA, it may be conjectured that the solid materials thus obtained (especially from NiCRA) should exhibit some unusual interesting electric and magnetic properties. Finally, although some hypotheses may be formulated, the actual reaction pathways for reductions by these reagents are still somewhat obscure.

We are currently undertaking some experiments likely to shed more light on the intriguing questions of the exact structure of CRA, their reaction pathways, and the physical properties of the solid materials obtained from them.