Complex reducing agents: their applications and their outcome in the field of carbonylations

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 $\frac{Abstract}{transfer} \ - \ Works \ performed \ in \ order \ to \ increase \ the \ single \ electron \ transfer \ ability \ of \ NaH \ and \ to \ decrease \ its \ basicity \ led \ us \ to \ discover \ new \ reagents : NaH-RONa-MX_{\Pi} \ called \ Complex \ Reducing \ Agents \ (CRA's).$ A short survey of the reducing properties of CRA's will be given. CRA's prepared in the presence of a ligand led to CRAL's which have proved to be good coupling reagents for aryl or vinyl halides (L = bpy). They also allowed the carbonylation (L = CO) of organic halides under standard pressure. These reactions opened up the field to phase-transfer-catalyzed photostimulated carbonylations as well as to SpN1 reactions of metalates.

INTRODUCTORY REMARKS CONCERNING THE REDUCING PROPERTIES OF NaH

Examination of the literature concerning NaH shows that this reagent is generally used, in organic chemistry, as a base for proton abstraction. However some data indicate that a few substrates may be reduced by this reagent. Though the yields of such reductions are often far from excellent, these results indicate the potential reducing properties of NaH which, unfortunately, are masked by the basic ones.

So, in order to use NaH as reducing agent, its single electron transfer (SET) ability must be increased and its basic properties must be masked.

Investigations undertaken in order to reach this target led us to discover new reducing agents possessing intriguing as well as interesting properties. In the present paper I shall give a brief survey of how we found these new reagents and I shall develop a few aspects of their properties (more informations may be obtained from reference (1)).

FROM NaH TO COMPLEX REDUCING AGENTS (NaH-RONa-MX_n) VIA NaH-RONa

A series of experiments performed with some organic halides and non-enolisable ketones showed that polar aprotic solvents (and particularly hexamethylphosphoric triamide (HMPA)) favorised SET from NaH but, of course, also increased the basic properties of this reagent (2).

In tetrahydrofuran (THF), NaH was very weakly reactive. However in the presence of sodium alkoxides prepared in situ (one of the best was sodium tert-amyloxide: \$\tanONa\$) a synergy appeared looking like the one discovered some years ago with NaNH2 (Complex Bases (3)). With NaH, an increase in the reactivity as well as in the SET ability was observed (2b,2c,2d,4). In fact, other things being equal, NaH-RONa in THF had comparable or even better reducing properties than NaH in HMPA.

Unfortunately NaH-RONa was still too basic to find general synthetic applications.

This problem was solved when we found that NaH-RONa reacted with a number of metal salts to give new reagents, we called Complex Reducing Agents (abbreviated CRA). Indeed CRA's were found weaker bases and stronger reducing agents than NaH-RONa. With most part of CRA's the differences observed between the two kinds of reagents were considerable. CRA's can be prepared starting from commercial reagents and starting from the halides or acetates of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Zr, Mo, Pd, W. Their properties mainly depend on the nature of the metal and in some degree on the nature of the alkoxide and of the solvent.

Note concerning the nomenclature of CRA's :

Complex Reducing Agents will be sometimes abbreviated as MCRA's (metal atom specified) or as RONa.MCRA's (alkoxide and metal atom specified). If necessary, we shall symbolize RONa.MCRA as NaH-RONa-MX $_{\rm n}$ although, of course, MX $_{\rm n}$ is not present as such in the reagent. The abbreviation RONa-MCRA (x/y/z) indicates that NaH/RONa/MX $_{\rm n}$ (in that order) is equal to

1876 P. CAUBÈRE

the molar ratio x/y/z. This ratio refers to the one of the starting reagents and has nothing to do with the actual constitution of the CRA.

About the real nature of CRA's, the situation is far from being clear, and we are only at the very beginning of their knowledge. For the present time only tBuONa.NiCRA (4/2/1) and tAmONa.ZnCRA (4/1/1) have been studied (5).

From the hydrogen evolution observed during the preparation and from X-ray powder patterns of the solid fractions the following conclusion may be drawn:

At least some tBuONa.NiCRA (if not all) is crystalline. From the data obtained this reagent appears to be constituted of aggregates formed by association of matrices consisting of Ni atoms surrounded by Na⁺, H⁻, $tBuO^-$, and perhaps AcO^- (the reagent was prepared from Ni(OAc)₂).

Concerning tAmONa.ZnCRA the situation is still less clear and it appeared that this reagent could be tentatively considered as a mixture of NaH [$(tAmO)_{X}Zn(Na)_{X}]_{n}$, a small amount of [$(tAmO)_{X}U(Na)_{X}U(N$

SOME GENERAL CONSIDERATIONS OF THE PROPERTIES OF CRA'S

The main interesting characteristics of CRA's may be summarized as follows:

- They are unexpensive reagents readily prepared from commercial grade starting materials. Thus it is sufficient to add, in a given solvent, anhydrous MX_{Π} to NaH-RONa or to add ROH to the suspension obtained by mixing NaH and MX_{Π} . The reagents are ready for use after short warming (6).
- The reducing properties being dependent on the nature of the metal, of the alkoxide and of the solvent, a palette of reducing agents with graduated properties can be obtained.
 Selective reduction can be thus performed.
- CRA's can constitute a source of metals in low degree of oxidation state. So they may be used in the preparation of selective catalysts for heterogeneous hydrogenation (7).

 Moreover, prepared in the presence of a ligand to quenche the metal species, they allow to prepare new reagents abbreviated CRAL or MCRAL (ligand specified) which some properties will be given below.

A SHORT VIEW ON THE REDUCING PROPERTIES OF CRA'S

Examplification of the reducing power which may be reached with CRA's is given in Scheme 1 where the reduction of aryl halides is reported (8).

Scheme 1

Besides the fact that substituted aryl chlorides and bromides are easily reduced, it must be emphasized that fluorides are also transformed without difficulty.

Of course primary, secondary, tertiary as well as vinyl halides (fluorides excepted) are also easily reduced. Moreover, using appropriate MCRA's, selective reductions can be performed (9).

Good illustration of the selectivity and versatility of CRA's was given with the reduction of carbonyl derivatives. It was found that in the presence of additive salts, such as MgBr₂, ketones and aldehydes were easily reduced by NiCRA or ZnCRA (10). Note that this property shows that CRA's are weak bases. Another interesting point also emerged from our studies. Indeed we showed that NiCRA's also reduced carbon-carbon double bond and, in certain cases, preferably to carbonyl group. The reverse was true with ZnCRA's which in fact were not able to reduce ethylenic linkage.

So we were encouraged to attempt the regionselective reduction of α,β -unsaturated ketones. A number of experiments are reported in Scheme 2 (11). They show that the regionselectivity of the unexpensive NiCRA's and ZnCRA's is such that they may be classified among the best reducing agents for this kind of reductions.

Scheme 2

Ni CRA-MgBr₂
THF, 20°C

R¹
THF, 20°C

R²
CH-CH
R³
R⁴

$$R^1 = R^4 = Me$$
, tBu ; $R^2 = R^3 = H$
 $R^1 = R^2 = R^4 = Me$; $R^3 = H$, $R^4 = Me$, Ph

 $R^1 = R^2 = R^4 = Me$; $R^3 = H$, $R^4 = Me$, Ph

 $R^1 = R^3 = H$; $R^2 = R^3 = H$; $R^4 = Me$, Ph

 $R^1 = R^3 = H$; $R^2 = R^3 = H$; $R^4 = Me$, Ph

 $R^1 = R^3 = H$; $R^2 = R^3 = H$; $R^4 = Me$, Ph

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 $R^1 = R^3 = H$; $R^2 = R^3 = H$; $R^4 = Me$, Ph

 $R^1 = R^3 = H$; $R^2 = R^3 = H$; $R^4 = Me$; $R^3 = H$; $R^4 = Me$, Ph

 $R^1 = R^3 = H$; $R^3 = H$;

The huge possibilities offered by CRA's in obtaining new reagents is well illustrated by the following results.

When Me_3SiCl was added to ZnCRA (12) an hydrosilylating agent (called ZnCRASi) was obtained. It very specifically hydrosilylated the carbonyl group of ketones and aldehydes as reported in Scheme 3.

Scheme 3

R1

R2

C=0
$$\frac{\text{ZnCRASi}}{\text{THF, } 20-25^{\circ}\text{C}}$$

R2

CH-0-SiMe₃

90-95 %

R1 = Me ; R2 = Me-(CH₂)₇, Me₂C=CH-(CH₂)₂, Ph

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(CH₂)₅, Ph, p.CIC₆H₄

R1 = H ; R2 = Me-(C

MCRAL'S AS SYMMETRICAL COUPLING REAGENTS OF ORGANIC HALIDES

During exploratory experiments, NiX $_2$ used in the preparation of CRA was replaced by (Ph $_3$ P) $_2$ NiCl $_2$. Interestingly, when the new reagent was tested against aromatic halides, we observed that the reducing properties were partially replaced by coupling properties. We supposed that in the presence of Ph $_3$ P (from (Ph $_3$ P) $_2$ NiCl $_2$) a fraction of the low oxidation state metal species was trapped as complexes capable to couple organic halides. In order to verify this hypothesis we first prepared \$\tauMONa.NiCRA (4/2/1) in the presence of Ph $_3$ P (4 equivalents). Addition of 1-bromonaphtalene to the reagent thus obtained (NiCRA-PPh $_3$) led to 70 % of 1,1'-binaphthyl and only 25 % of naphtalene (9a). The only drawback in this reaction was some classical transfer of phenyl group from Ph $_3$ P. In order to avoid this side

reaction, the phosphine was replaced by 2,2'-bipyridine (bpy) (2 equivalents). NiCRA (4/2/1) - bpy thus obtained coupled aryl halides with satisfying yields as it may be seen from Scheme 4 (9a, 13).

Note that the best results were obtained from aryl chlorides. Moreover aryl bromides are easily coupled even when an ortho substituent is present. Finally iodides led to the lowest yields. This behaviour is the reverse of what is observed when classical nickel reagents are used to couple aryl halides.

The side reduction may be slightly decreased using NiCRA (2/2/1) - bpy. However the reaction times were considerably increased.

A completely different situation was found with vinyl halides. Indeed, these halides were strongly reduced by NiCRA (4/2/1) - bpy and NiCRA (2/2/1) - bpy had to be used.

From the results reported in Scheme 5 it appears that our reagent is very efficient for the coupling of vinyl halides (13, 14).

Scheme 5

Coupling of vinyl halides by NiCRA (2/2/1) - bpy

It is also noteworthy that no isomerization occured during the coupling of cis- β -bromostyrene. However the side reduction can never be completely avoided and some reduced products were always formed.

An intriguing reaction we are still working on, was found. Thus for example when α -bromostyrene was put to react with NiCRA (2/2/1) - bpy in the presence of a small amount of THF in hexane, the only coupled product formed was 1,4-diphenyl butadiyne (Scheme 6).

Scheme 6

For the present time we have no rational explanation for this reaction which seems to take place with some other vinyl halides.

CARBONYLATION OF ORGANIC HALIDES WITH MCRACO'S UNDER STANDARD PRESSURE

Among the various ligands which could be of use in preparing MCRAL, carbon monoxide is of paramount interest. Indeed it might be expected that the corresponding reagents could be used in carbonylation reactions. We firstly chose to study the possible preparation of carbonyl cobalt species under standard pressure and their possible use in carbonylating aryl halides. These attempts were actual challenge since it was well known that preparations of carbonyl cobalt complexes from Co salts in aprotic media under mild conditions were rare. Moreover it was also known that extreme reaction conditions were required for carbonylation of aryl halides in the presence of Co species.

Careful systematic studies were necessary to succeed in preparing a series of reagents (called CoCRACO's) from CoCRA's (4/2/1) under standard pressure (15). We also showed that aryl halides (essentially bromides) were reproducibly carbonylated under atmospheric pressure of CO. A mixture of esters and acid were obtained in excellent yields (Scheme 7).

Scheme 7

Z

Br
$$\frac{tBuCH_2ONa.CoCRACO}{CO (P atm), THF, 63°C}$$

then H_3O^+

Z

COOCH₂ $tBu + Z$

COOCH₂ $tBu + Z$

RO-100 %

$$Z = H$$
, $2-Me$, $3-Me$, $4-Me$, $2-MeO$, $3-MeO$, $4-MeO$, $4-F$, $4-MeCO$

Note that in the presence of amines, amides were obtained in moderate to good yields. Moreover this reactions were highly catalytic in cobalt.

When we investigated the constitution of CoCRACO's we found that 90 % of the cobalt was in solution but that only a fraction (ca 9 to 13 %) of the soluble cobalt was as carbonyl species. Much more surprising was the finding that the only carbonyl cobalt species present was NaCo(CO) $_4$ (16). Indeed it was well known that this anion was not able to carbonylate aryl halides under mild conditions. We showed that this apparent contradiction was due to the presence of NaH. We interpreted this observation by an $S_{\mbox{RN}}^{\mbox{N}}$ 1 mechanism initiated by SET from H (Scheme 8).

Scheme 8

[Electron Source] + Ar-X
$$\longrightarrow$$
 [Ar-X]⁻ \longrightarrow Ar' + X⁻

Ar' + Co(CO)₄ \longrightarrow [Ar-Co(CO)₄]⁻ \longrightarrow [Ar-X]⁻ + ArCo(CO)₄
 \longrightarrow etc...

Ar-Co(CO)₄ \longrightarrow Products

1880 P. CAUBÈRE

This hypothesis seems supported by the fact that we were able to photostimulate the carbonylation of aryl halides in the presence of $NaCo(CO)_4$ -tAmoNa (16). In these reactions NaH was replaced by light. We shall see later an interesting consequence of these experiments.

Starting from FeCl $_3$ we were also able to prepare tAmONa.FeCRACO under standard pressure of CO (17). The soluble fraction contained mainly Na₂Fe(CO) $_4$ and some Na₂Fe $_2$ (CO) $_8$. Parallel to what we observed with Co, we showed that the behaviour of FeCRACO was very different from the behaviour of pure Na₂Fe(CO) $_4$ studied by Collman. Thus primary, secondary and even some tertiary bromides and chlorides were carbonylated by FeCRACO under atmospheric pressure of CO (Scheme 9).

Scheme 9

On the contrary it is well known that under normal conditions $Na_2Fe(CO)_4$ itself is only moderately reactive with secondary halides and that no reaction is observed with 1-bromo adamentane.

Note that the carbonylations of primary and secondary halides by FeCRACO were catalytic in metal.

A radical mechanism must also be suspected for most of these carbonylations. This seems supported by the carbonylation (40 % yield) of C_6H_5Br by FeCRACO under standard pressure of CO (17).

AN INTERESTING CONSEQUENCE OF THE STUDIES OF MCRACO IN THE FIELD OF THE CARBONYLATIONS UNDER PHASE TRANSFER CATALYSIS (PTC) CONDITIONS

The success in carbonylating aryl halides with $\mathrm{Na}^+\mathrm{Co}(\mathrm{CO})_4^-$ was due to the fact that this metalate was able to react via an S_{RN} 1 process. On the other hand it was known that $\mathrm{Co}(\mathrm{CO})_4^-$ might be generated from $\mathrm{Co}_2(\mathrm{CO})_8^-$ in a PTC process. However, under these conditions only organic halides which are particularly reactive in SN_2 process can be carbonylated. Our results led us to think that simple irradiation of such systems might allow the carbonylation of aryl and vinyl halides under standard pressure.

This was in fact the case, and we showed in a first series of experiments, that aryl and vinyl halides can be carbonylated by irradiating a PTC system in a pyrex reaction flask with a simple commercial "sun lamp" (18) (Scheme 10).

Scheme 10

R-X
$$\frac{\text{Co}_2(\text{CO})_8 \text{ (Catal.), CO (P atm), C}_6\text{H}_6/\text{NaOH (aq.) or}}{\text{NaOH (aq.), Bu}_4\text{NBr (Catal.), hv (sun lamp), 63°C}}$$
RCOOH 95-98 % then H_3O^+

X = Br R = C_6H_5 , $2\text{-MeC}_6\text{H}_4$, $4\text{-MeC}_6\text{H}_4$, $4\text{-MeOC}_6\text{H}_4$, $4\text{-FC}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, $4\text{-Cl$

$$X = C1$$
 $R = 1$ -cyclohexenyl, t Bu- C = CH_2

70 %

As an extension of these results we were able to prepare benzolactams and lactones (Scheme 11) starting from aryl halides bearing amino or hydroxy groups on a side chain α to the halogen.

Scheme 11

In any case, the results obtained compare very favourably with those obtained with palladium species. Indeed the present method is much less expensive, the reactions are carried out under milder conditions and yields are of the same magnitude and often higher.

A number of observations carried out during these studies also led us to show that benzyl and allyl triethylammonium salts can be carbonylated under PTC conditions by photostimulated $S_{\text{RN}}\mathbf{1}$ process (19). The results obtained are reported in Scheme 12.

Scheme 12

n = 1

R = Et

1882 P. CAUBÈRE

CONCLUSION

We started from NaH and we showed that this hydride can donate its electrons, but its proton affinity impedes from using it as a SET reagent in organic chemistry. When activated by alkoxides its SET tendency becomes better but the basicity of NaH-RONa still constitutes a considerable drawback.

In CRA's a synergism between NaH-RONa and metal species seems to arise, the result of which being the formation of a weak basic reagent possessing a strong ability in donating electrons to organic substrates.

This brief survey on some of the properties of CRA's shows how rich their chemistry is. In fact we are far from having exhausted the possibilities they offer.

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