Journal of Organometallic Chemistry, 264 (1984) 263–271
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS

XIX *. HOMO COUPLING OF ARYL AND VINYL HALIDES PROMOTED BY LIGAND MODIFIED NiCRA (NaH–RONa–Ni(OAc)$_2$) **

RÉGIS VANDERESSE, JEAN-JACQUES BRUNET and PAUL CAUBERE*
Laboratoire de Chimie Organique I, ERA CNRS No. 476, Université de Nancy I Boîte Postale 239, 54506 Vandoeuvre-les-Nancy Cédex (France)

(Received April 6th, 1983)

Summary

The preparation of NiCRA (NaH–t-AmONa–Ni(OAc)$_2$) in the presence of 2,2′-bipyridine (bpy) leads to a new reagent (termed NiCRA-bpy) which is shown to be one of the most efficient Ni based reagents reported so far for the homocoupling of aryl and vinyl halides (including chlorides). The homo coupling of *cis*- and *trans*-β-bromostyrenes is shown to be stereospecific.

Metal promoted homo coupling of aryl and vinyl halides continues to be actively studied [2] on account of its wide range of synthetic applications [3–7]. The literature reveals that nickel(0) complexes (such as Ni(COD)$_2$ [2] or Ni(PPh$_3$)$_4$ [8]) or activated metallic nickel [9] can be used to perform this kind of reaction, but the nickel based reagents reported so far suffer from some disadvantages. For example, most of these nickel complexes are highly air sensitive [8] and some of them, such as Ni(COD)$_2$ are very heat sensitive [2]. When these nickel-based reagents are used with aryl halides, although coupling of aryl iodides is reported to occur in fair to good yield, coupling of aryl bromides is sometimes less successful, and no efficient coupling of aryl chlorides has been reported previously [2]. Moreover, the presence of *ortho* substituents severely impedes the coupling of aryl bromides [2,8]. In the case of coupling of vinyl halides, nickel(0) complexes have been reported to promote the coupling of vinyl bromides with moderate efficiency [2]. However these reactions are not stereoselective in the case of simple vinyl bromides [2]. Furthermore, no couplings of simple vinyl chlorides have been reported [2].

In the present paper, we wish to describe the preparation and use of new

---

* For part XVIII see ref. 1.

** Dedicated to Prof. R. Calas on the occasion of his 70th birthday.

nickel-based reagents [10] which allow the homo coupling of aryl and vinyl halides without the above limitations.

Results and discussion

Sodium hydride containing complex reducing agents "NaH–RONa–MX_n" (abbreviated MCRA, where M is a transition metal, Zn, or Cd) [11], developed some years ago in this laboratory have already found several applications in organic synthesis [12–16]. In the case of organic halides, NiCRA has been shown to be a very efficient system for the reduction of alkyl, and aryl halides and for the stereospecific reduction of vinyl halides [12].

Our previous hypotheses [10] of the presence of low oxidation state metal species in CRA has recently been confirmed for the nickel and zinc based reagents [1]. Indeed, it has been found that both reagents are constituted of metal(0) species surrounded by NaH and RONa moieties. It is also now well established that the presence of sodium hydride and alkoxide plays a key role in the unique properties of MCRA [11]. These observations led us to conjecture that the preparation of NiCRA in the presence of suitable ligands could possibly lead to new reagents containing nickel(0) complexes, the properties (and stability) of which would be modified by the presence of NaH and/or RONa. The results reported here completely confirm this hypothesis.

For convenience, these new reagents will be referred to as NiCRAL (x,y,z,t), where L indicates the nature of the ligand used and (x,y,z,t) represents the molar ratio of (NaH,RONa,MX_n,L) involved in the preparation of the reagent.

In the present work, all coupling reagents were prepared using t-AmONa as activating agent. The ligands used were either Ph_3P or 2,2′-bipyridine (bpy).

Preparation of NiCRA-PPh_3(4,2,1,4) and NiCRA-bpy(4,2,1,2)

Both reagents were easily prepared (see Experimental) by addition of t-AmOH (20 mmol) to a THF suspension of NaH (60 mmol) and $Ni(OAc)_2$ (10 mmol) containing PPh_3 (40 mmol) or bpy (20 mmol). On the above nomenclature, these reagents are termed NiCRA-PPh_3(4,2,1,4) and NiCRA-bpy(4,2,1,2), since 20 mmol NaH are consumed to form t-AmONa (20 mmol).

The volume of hydrogen evolved during the preparation of these reagents

TABLE 1

COUPLING OF ARYL HALIDES WITH NiCRA-PPh_3(4,2,1,4) [a]

ArX	Reaction time (h)	Ar–Ar (%) [b]	ArH (%) [c]	ArC_6H_5 [b]
$C_{10}H_7Br$ [e]	0.5	85	10	3 (*d*)
C_6H_5Br	0.5	70	60	–
C_6H_5Cl	7.5	90	47	–
4-MeC_6H_4Cl	5	63	22	12
4-$MeOC_6H_4Br$	1.5	60	15	15

[a] Reactions performed at 63°C in THF on a 10 mmol scale with a molar ratio $Ni(OAc)_2/ArX = 1$ (see experimental section). [b] Isolated yields. [c] Determined by GC analysis with internal standards. [d] The presence of small amounts of biphenyl was also observed (GC analysis). [e] 1-Bromonaphthalene.

TABLE 2

COUPLING OF ARYL HALIDES WITH NiCRA-bpy(4,2,1,2) [a]

ArX	Reaction time	Ar–Ar (%) [b]	ArH (%) [c]
C_6H_5I	3 min	40 (37)	46 [d]
C_6H_5Br	30 min	76 (70)	20
C_6H_5Cl	2.5 h	90 (86)	8
$C_{10}H_7I$ (*e*)	10 min	66 (62)	26
$C_{10}H_7Br$ (*e*)	15 min	74 (70)	23
$C_{10}H_7Cl$ (*e*)	20 min	90 (88)	8
2-$MeOC_6H_4Br$	30 min	69 (66)	30
3-$MeOC_6H_4Br$	30 min	75 (71)	21
4-$MeOC_6H_4Br$	30 min	78 (75)	17
4-$MeOC_6H_4Cl$	8 h	79 (73)	16
2-MeC_6H_4Cl	8 h	84 (82)	15
3-MeC_6H_4Cl	8 h	80 (75)	23
4-MeC_6H_4Cl	8 h	80 (75)	12
4-MeC_6H_4Br	45 min	70 (70)	30

[a] Reactions performed on a 10 mmol scale in THF at 63°C with a Ni/ArX ratio of 1. [b] Determined by GC analysis. Isolated yields in parentheses. [c] Determined by GC analysis with internal standards. [d] The presence of small amounts of 2-phenyl tetrahydrofuran was observed by GC analysis. [e] 1-Halonaphthalene.

corresponded to the expected reaction of NaH with t-AmOH (i.e. 20 mmol) and to the reduction of nickel(II) to nickel(0) (i.e. 10 mmol) according to eq. 1.

$$2\ H^- + Ni^{II} \rightarrow Ni^0 + H_2 \qquad (1)$$

From our previous work on this topic [1], it can be concluded that these two NiCRA-L contain NaH (20 mmol), Ni^0 (10 mmol), t-AmONa (20 mmol) and either Ph_3P (40 mmol) or bpy (20 mmol).

Coupling of aryl halides by NiCRA-PPh_3(4,2,1,4) and NiCRA-bpy(4,2,1,2)

The first experiments were performed with NiCRA-PPh_3 using 1-bromonaphthalene as a test case. These experiments revealed some important features of the reaction: (i) in 1,2-dimethoxyethane, a classical solvent for NiCRA [11], no coupling occurred and the only reaction observed was reduction to naphthalene (ii) in contrast, in THF coupling to give 1,1′-binaphthyl took place showing that the presence of a ligand during the preparation of NiCRA led to new reagents which exhibited coupling ability. It should be remembered that in the absence of an added ligand only reduction was observed [12]; (iii) the best coupling yields were obtained with a $Ni(OAc)_2/PPh_3$ molar ratio of 4; and, (iv) thorough examination of the reaction products indicated that, besides 1,1′-binaphthyle and naphthalene, small amounts of 1-phenylnaphthalene and biphenyl were formed.

The best conditions determined in this way were used for the coupling of some aryl halides. As may be seen from Table 1, yields of Ar–Ar coupled products were good. However, some phenyl transfer also occurred, leading to ArC_6H_5 side products. This side reaction resembles the previously reported phenyl transfer (from PPh_3 to the nickel centre) which has been found to occur, for instance, in the thermal decomposition (80°C) of $ArNi(Cl)(PPh_3)_2$ [17,18], and suggests the intervention of such intermediate in the present coupling reactions.

TABLE 3

COUPLING OF ARYL HALIDES BY NiCRA-bpy(2,2,1,2) [a]

ArX [a]	ArX/Ni ratio	Reaction time (min)	Ar–Ar (%) [b]	ArH (%) [c]
C_6H_5I	1	20	50	30 [d]
	0.5	15	42	35 [d]
C_6H_5Br	1	210	81	15
	0.5	40	84	11
C_6H_5Cl	1	390	65	[e]
	0.5	210	84	10
2-$MeOC_6H_4Br$	1	120	76 (72)	24
	0.5	35	79 (77)	21
4-MeC_6H_4Br	1	120	80 (74)	18
	0.5	30	84 (80)	15

[a] Reactions performed at 63°C in THF in a 10 mmol $Ni(OAc)_2$ scale and either 10 mmol or 5 mmol ArX (see ArX/Ni ratio). [b] Determined by GC analysis with internal standards. Isolated yields in parentheses. [c] Determined by GC analysis with internal standards. [d] Formation of 2-phenyltetrahydrofuran was observed by GC. [e] 30% recovered starting chlorobenzene (GC analysis).

In order to avoid this side reaction, PPh_3 was replaced by the bidentate ligand 2,2′-bipyridine. (Under the conditions used in this work, use of 1,5-COD led to a reagent which exhibited no coupling ability towards aryl halides). The results obtained with this new reagent, NiCRA-bpy(4,2,1,2), are summarized in Table 2. As can be seen from that Table, except in one case, biaryls were obtained in good yields. One of the main features of these results is that, contrary to what is reported to occur with the more usual nickel based reagents [2,8], the best yields of biaryls were obtained from aryl chlorides. Some supplementary experiments conducted with iodobenzene showed that lowering the reaction temperature to 20°C did not improve the yield of biphenyl. Whatever the temperature, a significant amount of benzene was formed. Moreover, besides benzene, 2-phenyltetrahydrofuran was formed in up to 15% yield, indicating the intervention of phenyl radicals during the reaction. However the reaction pathway by which these radicals are formed is not clear.

Finally, it must be emphasized that, again in contrast with classical nickel based reagents [2], NiCRA-bpy brought about the efficient coupling of aryl bromides and chlorides bearing *ortho* substituents.

The above results underline the special properties of NiCRA-bpy, which is clearly more efficient than the previously used nickel-based coupling reagents.

Coupling of aryl halides with NiCRA-bpy(2,2,1,2)

From the above results, two questions arose: first, was the NaH still present (vide supra) in NiCRA-bpy(4,2,1,2) necessary for the coupling to take place? Secondly, could the reduction to ArH be avoided by using a smaller amount of NaH (that is 40 mmol instead of 60 mmol)?

To answer these questions, we prepared NiCRA-bpy(2,2,1,2). The volume of hydrogen evolved during this preparation indicated that the resulting reagent was free of any hydride and thus contained only Ni^0 (10 mmol), t-AmONa (20 mmol) and bpy (20 mmol).

The behaviour of this new reagent toward C_6H_5X (X = I, Br, Cl) was examined, as was its effectiveness in the case of the two substituted aryl halides which gave lower yields of biaryls with NiCRA-bpy(4,2,1,2).

As may be seen from Table 3, the non-hydridic NiCRA-bpy allowed the coupling of aryl halides in good yield, and even in generally slightly better yields than NiCRA-bpy(4,2,1,2). However, reaction times necessary to assure total conversion of the aryl halides were much longer. Nevertheless, it is clear that the presence of hydride species is not necessary for the coupling to occur. The answer to the second question is also quite clear and it is apparent that hydrogenolysis of C–X bonds is diminished (compare with Table 2). This indicates that with NiCRA-bpy(4,2,1,2) part of the reduction to ArH was due to the hydride species included in the reagent. Nevertheless, in agreement with the conclusions reached by Kochi [19], it is clear that part of the reduction must be due to the formation of aryl radicals during the coupling process.

From a mechanistic point of view, results in the literature [19,20] suggest that nickel(0) species constitute the active species for all these coupling reactions. If we assume that the active metal species are the same in both reagents, comparison of the results obtained with NiCRA-bpy(4,2,1,2) and those obtained with NiCRA-bpy(2,2,1,2) indicates that in the former reagent the concentration of active metal species is higher during the reaction; in other words, the hydride species present in NiCRA-bpy(4,2,1,2) may promote (at least partially) some regeneration of the active nickel(0) species. This hypothesis is supported by the fact that the coupling of aryl halide with NiCRA-bpy(2,2,1,2) is more rapid when ArX/Ni = 0.5 than when ArX/Ni = 1 (Table 3). An alternative possibility, which cannot usefully be discussed in the present state of our knowledge, would be that the active species are not the same in NiCRA-bpy(4,2,1,2) and in NiCRA-bpy(2,2,1,2).

TABLE 4

COUPLING OF VINYL HALIDES BY NiCRA-bpy(2,2,1,2)

Vinyl halide [a]	Method [b]	T(°C)	Reaction time (h)	Product (%) [c]
1-Bromocyclooctene	A	63	0.5	1-(cycloocten-1-yl)cyclooctene (87)
1-Bromocyclooctene	B	40	1	1-(cycloocten-1-yl)cyclooctene (83)
1-Chlorocyclohexene	A	63	1.5	1-(cyclohexen-1-yl)-cyclohexene (80)
1-Chlorocyclohexene	B	40	2	1-(cyclohexen-1-yl)-cyclohexene (80)
trans-β-bromostyrene	A	30	2	(t,t)-1,4-diphenyl--1,3-butadiene (75)
trans-β-bromostyrene	B	40	2	(t,t)-1,4-diphenyl--1,3-butadiene (85)
cis-β-bromostyrene	A	30	2	(c,c)-1,4-diphenyl--1,3-butadiene (75)
cis-β-bromostyrene	B	40	2	(c,c)-1,4-diphenyl--1,3-butadiene (75)

[a] Reactions performed on a 10 mmol vinyl halide scale with a Ni/vinyl halide molar ratio of 1 (see experimental section). [b] Method A: reactions performed in pure THF (50 ml). Method B: reactions performed in 50 ml hexane in the presence of 40 mmol THF. [c] Isolated yields after purification by column chromatography.

Coupling of vinyl halides with NiCRA-bpy(4,2,1,2) and NiCRA-bpy(2,2,1,2)

Exploratory experiments were conducted in THF with NiCRA-bpy(4,2,1,2) using 1-bromocyclooctene as a test case. The results obtained showed that the coupled product were obtained in only moderate yields, hydrogenolysis of the C–Br bond being the major side reaction.

In contrast, as can be seen from Table 4, NiCRA-bpy(2,2,1,2) was found to be particularly efficient for the coupling of vinyl halides (molar ratio Ni/vinyl halide = 1). The reasons for the difference in behaviour between aryl and vinyl halides toward these two NiCRA-bpy species are not obvious.

Interestingly, during the course of this study, it was found that these reactions can be performed using hexane as solvent provided that 40 mmol of THF are present. Use of this new medium (Method B, see Experimental Section) leads to the same yields as those obtained in pure THF (see Table 4).

It must be emphasized that even simple vinyl chlorides were efficiently coupled. To the best of our knowledge such a reaction has not previously been reported with other nickel based coupling reagents. It is also noteworthy that no isomerization occurred during the coupling of *cis*-β-bromostyrene.

This observation seems to indicate that free vinyl radicals are not involved [21] during the formation of the coupled product which must arise from vinylnickel species. Such a stereospecificity cannot be obtained (at least in the case of simple vinyl halides) with Ni(COD)$_2$-based reagents [2].

NiCRA-bpy(2,2,1,2) thus appears to be one of the best Ni based reagents so far examined for the homo coupling of vinyl halides.

Conclusion

The present work shows that NiCRA-L (the structure of which has not yet been elucidated) allow very efficient coupling of aryl halides, including chlorides. The presence of *ortho* substituents does not impede the reaction. Coupling of simple vinyl bromides and chlorides is also very efficient and, at least in the cases studied, is stereospecific. These results strongly support the suggestion of the presence of nickel(0) species in NiCRA-L.

In comparison with other Ni based reagents the special properties of NiCRA-L seems to be due to the presence of sodium alkoxides. These results underline, once again, the very great effect of alkoxides in such reaction media [22].

Experimental

Materials

Fluka (or Degussa) sodium hydride (55–60% in oil) was used after three washings with the reaction solvent under nitrogen. Each batch of sodium hydride was titrated by standard techniques [23] before use. Badische Anilin reagent grade THF was distilled from a benzophenone-sodium adduct and stored over sodium wires. DME (Fluka) was distilled from sodium. For both solvents, the absence of peroxides was checked before each run. Hexane was distilled from KMnO$_4$. t-Amyl alcohol was distilled from sodium. Nickel acetate (Prolabo) was dried in vacuo for 12 h at 120–125°C. Triphenylphosphine and 2,2′-bipyridine (Fluka) were used without further purification. All organic halides were either purchased (Fluka or Aldrich) or prepared by standard procedures (1-chlorocyclohexene [24], 1-bromocyclooctene [25], *cis*-β-bromostyrene [26]). All reactions were carried out under nitrogen (nitrogen ®, L'Air Liquide). Silica column chromatography was performed using Woelm silicagel (0.063–0.200 mm) with petroleum ether/ether mixtures as eluent.

General

GC analysis were performed on either a Carlo–Erba (GI 452) or a Girdel (300 or 3000) apparatus (flam-ionisation detector) equipped with 5 m length columns. IR spectra were recorded on a Perkin–Elmer spectrophotometer (model 580 B) and NMR spectra on a Perkin–Elmer R12B instrument.

Coupling of aryl halides by NiCRA-PPh$_3$(4,2,1,4): Table 1 and NiCRA-bpy(4,2,1,2): Table 2: General procedure

t-AmOH (20 mmol) in 10 ml THF was added dropwise to a suspension of NaH (60 mmol), Ni(OAc)$_2$ (10 mmol) in refluxing THF (30 ml) containing Ph$_3$P (40 mmol) or bpy (20 mmol). After 2 h stirring at 63°C, the reagent was ready for use. The aryl halide (10 mmol) was then added along with the internal standard (hydrocarbons C_8–C_{14}) and 10 ml of THF, and the reaction was monitored by GC analysis of small aliquots taken by syringe. GC analyses were performed on the following 5 m columns (temperatures): halogenonaphthalenes and naphthalene: QF$_1$ (200°C); halogenobenzenes: SE 30 (150°C); benzene: Carbowax 20M (90°C); halogenotoluenes: QF$_1$ (220°C); toluene: Carbowax 20M (110°C); halogenoanisoles: QF$_1$ (220°C); anisole: QF$_1$ (130°C).

After completion of the reaction, the flask was cooled to 0°C. The excess hydride was then carefully destroyed by dropwise addition of either EtOH or EtOH/water mixtures until hydrogen evolution ceased. The mixture was then acidified, and the organic phase was extracted into diethyl ether and dried over MgSO$_4$. After removal of solvents under reduced pressure, the products were separated by chromatography on silica columns. They were characterized either by direct comparison (m.p., IR, NMR) with authentic samples (1,1'-binaphthyl, 1-phenylnaphthalene, biphenyl, 2-phenyltetrahydrofuran, 4-methylbiphenyl, 4-methoxybiphenyl) or by comparison of their properties (m.p., ^{1}H NMR, IR, UV) with those reported in the literature (2,2'-dimethylbiphenyl, 3,3'-dimethylbiphenyl and 4,4'-dimethylbiphenyl [27,28], 2,2'-dimethoxybiphenyl, 3,3'-dimethoxybiphenyl, 4,4'-dimethoxybiphenyl) [27,28].

Coupling of aryl halides by NiCRA-bpy(2,2,1,2): Table 3

The same procedure and quantities as above were used except that the reagent was prepared from only 40 mmol NaH. As indicated in the Table, reactions were performed with either 5 or 10 mmol aryl halide. The reaction was then monitored and the products isolated as above.

Coupling of vinyl halides by NiCRA-bpy(2,2,1,2): Table 4

Method A: The reagent was prepared following the general procedure from NaH (40 mmol), Ni(OAc)$_2$ (10 mmol), t-AmOH (20 mmol) and bpy (20 mmol) in 40 ml THF.

Method B: The reagent was prepared as for method A but the 40 ml of THF were replaced by a mixture of 40 ml hexane and 40 mmol THF.

With either method, the reaction was monitored by GC analysis of small aliquots.

The GC analyses were performed on the following 5 m columns (temperature): 1-bromocyclooctene and 1,1′-bicyclooctenyl: OV 101 (temperature programmation: 80–180°C), 1-chlorocyclohexene and 1,1′-bicyclohexenyl: OV 101 (temperature programmation: 80–150°C), β-bromostyrenes: OV 101 (120°C).

After completion, the usual work-up and separation procedures gave the coupled products, which were identified by comparison of their spectroscopic properties (^{1}H NMR, IR and UV) with those reported in the literature [29,30,31].

Acknowledgement

We thank the Centre National de la Recherche Scientifique, France (ATP: Messagers Chimiques) for support of the research. We also thank the Degussa (Germany) company for a gift of sodium hydride.

References

1 J.J. Brunet, D. Besozzi, A. Courtois and P. Caubere, J. Am. Chem. Soc., 104 (1982) 7130.

2 See for example: M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L. Speltz Ryono, J. Gorzynski Smith, and R.D. Stauffer, J. Am. Chem. Soc., 103 (1981) 6460 and ref. cited therein

3 For recent reviews see: (a) J.F. Normant, Synthesis, (1972) 63; (b) M. Goshaev, O.S. Osteroshchenko, and A.S. Sadykok, Russ. Chem. Rev. (Engl. Trans.), (1972) 1046; (c) P.E. Fanta, Synthesis (1974) 9; (d) A.E. Jukes, Adv. Organomet. Chem., 12 (1974) 215.

4 F. Ullmann and J. Bielecki, Chem. Ber., 34 (1901) 2174.

5 (a) T. Cohen and I. Cristea, J. Am. Chem. Soc., 98 (1976) 748; (b) J. Cornforth, A.F. Sierkowski, and T.W. Wallace, J. Chem. Soc., Chem. Commun., (1979) 294; (c) R.D. Rieke and L.D. Rhyne, J. Org. Chem., 44 (1979) 3445.

6 For examples and leading references, see: F.E. Ziegler, I. Chliver, K.W. Fowler, S.J. Kanfer, S.J. Kuo, and N.D. Senha, J. Am. Chem. Soc., 102 (1980) 790.

7 T. Cohen and I. Cristea, J. Org. Chem., 40 (1975) 3649.

8 (a) A.S. Kende, L.S. Liebeskind, and D.M. Braitsch, Tetrahedron Lett., (1975) 3375; (b) M. Zembayashi, K. Tamao, J.-I. Yoshida, and M. Kumada, ibid., (1975) 4089. See also: K. Takagi, N. Hayama, and S. Inokawa, Chem. Lett., (1979) 917, and Bull. Chem. Soc. Jpn, 53 (1980) 3691.

9 S.-I. Inaba, H. Matsumoto, and R.D. Rieke, Tetrahedron Lett., (1982) 4215.

10 A short preliminary note appeared on these new reagents: B. Loubinoux, R. Vanderesse and P. Caubere, Tetrahedron Lett., (1977) 3951.

11 J.J. Brunet, R. Vanderesse and P. Caubere, J. Organomet. Chem., 157 (1978) 125.

12 (a) Reduction of aryl halides: G. Guillaumet, L. Mordenti and P. Caubere, J. Organomet. Chem. 92 (1975) 43; (b) Reduction of alkyl and vinyl halides: G. Guillaumet, L. Mordenti, and P. Caubere, ibid., 102 (1975) 353; R. Vanderesse, J.J. Brunet, and P. Caubere, J. Org. Chem., 46 (1981) 1270.

13 Reduction of carbonyl compounds: J.J. Brunet, L. Mordenti and P. Caubere, J. Org. Chem., 43 (1978) 4804; J.J. Brunet, D. Besozzi, and P. Caubere, Synthesis, (1982) 721; L. Mordenti, J.J. Brunet, and P. Caubere, J. Org. Chem., 44 (1979) 2203.

14 Reduction of C–C multiple bonds: J.J. Brunet, L. Mordenti, B. Loubinoux, and P. Caubere, Tetrahedron Lett., (1977) 1069; J.J. Brunet and P. Caubere, ibid., (1977) 3947.

15 Preparation of heterogeneous hydrogenation catalysts: J.J. Brunet, P. Gallois, and P. Caubere, Tetrahedron Lett., (1977) 3955; J.J. Brunet, P. Gallois, and P. Caubere, J. Org. Chem., 45 (1980) 1937; P. Callois, J.J. Brunet, and P. Caubere, ibid., 45 (1980) 1946.

16 Preparation of new carbonylation cobalt and iron catalysts: J.J. Brunet, C. Sidot, B. Loubinoux and P. Caubere, J. Org. Chem., 44 (1979) 2199; J.J. Brunet, C. Sidot and P. Caubere, ibid., 46 (1981) 3147; J.J. Brunet, C. Sidot and P. Caubere, J. Organomet. Chem., 204 (1980) 229.

17 A. Nakamura and S. Otsuka, Tetrahedron Lett., (1974) 463. See also D.R. Fahey and J.E. Mahan, J. Am. Chem. Soc., 98 (1976) 4499.

18 S. Otsuka, A. Nakamura, T. Yoshida, N. Naruto and K. Ataka, J. Am. Chem. Soc., 95 (1973) 3180.

19 T.T. Tsou and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 6319.
20 T.T. Tsou and J.K. Kochi, J. Am. Chem. Soc., 101 (1979) 7547.
21 S.K. Chung, J. Org. Chem., 45 (1980) 3513.
22 P. Caubere, Top. Curr. Chem., 73 (1978) 50 and ref. cited therein.
23 J. Plesek and S. Hermanek, Sodium Hydride, Iliffe, London, 1968.
24 M. Mousseron and R. Jacquier, Bull. Soc. Chim. Fr., (1950) 648.
25 P. Caubere and G. Coudert, Bull. Soc. Chim. Fr., (1973) 3067.
26 S.J. Cristol and P. Norris, J. Am. Chem. Soc., 75 (1953) 2645.
27 Handbook of Chemistry and Physics, 47th edition, The chemical Rubber Co, Cleveland, 1966-1967.
28 J.G. Grasseli, Atlas of spectral data and physical constants for organic compounds, Chemical Rubber Co, Cleveland, 1973.
29 G. Laber, Liebigs Ann. Chem., 588 (1954) 79.
30 H. Lunde and L. Zechmeister, Acta Chem. Scand., 8 (1954) 1421.
31 J.K. Pinckard, B. Wille and L. Zechmeister, J. Am. Chem. Soc., 70 (1948) 1938.