Electrochemically induced chain reactions. Reactions of aromatic aldehydes induced by electrogenerated bases

Michaël Bernard,[a] Dominique Lucas,[a] Bernard Hanquet,[a] Yves Mugnier[a],* and Jean Lessard[b],*

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (CNRS UMR 5632), Faculté des Sciences Gabriel, Université de Bourgogne, 21000 Dijon, France. E-mail: Yves.Mugnier@u-bourgogne.fr*

[b] *Laboratoire d'Electrochimie et d'Electrocatalyse, Département de Chimie, Université de Sherbrooke, Sherbrooke, QUE, J1K 2R1, Canada. E-mail: JLessard@courrier.usherb.ca.*

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The electrochemical reduction of aromatic aldehydes (ArCHO) such as 2-naphthaldehyde (**1**), 4-dimethylaminobenzaldehyde (**2**), 3-methoxybenzaldehyde (**3**) and 2-pyrrole carboxaldehyde (**4**) in *N*,*N*-dimethylformamide with tetrabutylammonium hexafluorophosphate as supporting electrolyte, under an argon atmosphere and in the presence of protons donors (AH_2) such as fluorene (FlH_2) or indene (InH_2), gives products such as (ArCH=A) and/or [$ArCH(AH)_2$] (AH = FlH or InH). Three consecutive chain reactions are initiated by proton abstraction from fluorene or indene by a base electrogenerated by the reduction of ArCHO. The propagation steps of the first chain reaction involves addition of AH^- to ArCHO and protonation of the resulting alcoholate with regeneration of AH^- to give the carbinol ArCH(OH)AH. The second chain reaction is the base-catalyzed dehydration of ArCH(OH)AH to ArCH=A. The third is the addition of AH^- to ArCH=A, giving $ArCH(AH)_2$ with regeneration of AH^-.

Réactions en chaîne induites électrochimiquement. Réactions d'aldéhydes aromatiques induites par des bases électrogénérées. La réduction électrochimique d'aldéhydes aromatiques (ArCHO) tels que le 2-naphtaldéhydes (**1**), le 4-diméthylaminobenzaldéhyde (**2**), le 3-méthoxybenzaldéhyde (**3**) et le 2-pyrrolecarboxaldehyde (**4**) en présence d'hexafluorophosphate de tétrabutylammonium comme électrolyte support sous l'influence de donneurs de protons AH_2 tels que le fluorène (FlH_2) ou l'indène (InH_2) conduit aux composés ArCH=A et (ou) $ArCH(AH)_2$ (AH = FlH ou InH). Trois réactions en chaîne consécutives sont initiées par abstraction d'un proton de AH_2 par la base électrogénérée par réduction de ArCHO. L'étape de propagation de la première réaction en chaîne correspond à l'addition de l'anion AH^- sur l'aldéhyde ArCHO suivie de la protonation de l'alcoolate résultant par AH_2 pour conduire à l'alcool ArCH(OH)AH avec régénération de AH^-. La seconde réaction en chaîne correspond à la déshydratation de ArCH(OH)AH en ArCH=A sous l'influence de la base AH^-; enfin la formation de $ArCH(AH)_2$ s'effectue par addition de AH^- sur ArCH=A suivie d'une protonation par AH_2.

Reaction of organic products in suitable medium affords highly basic and/or nucleophilic reagents that may find some use in organic synthesis. Particularly, electrogenerated bases have been reported to induce chain reactions. The addition of geminal polyhalocarbanions to activated olefins,[1] the reaction of oxygen with electrogenerated fluorenyl anion to give fluorenone,[2] the electrocatalyzed elimination of methanol from 9-methoxybifluorenyl,[3] and Michael reactions[4] are representative examples.

In the latter case the donor Don-H containing an acidic hydrogen atom is deprotonated by the base giving the anion Don^-, which adds to the acceptor, for example an activated olefin. The resulting anionic adduct deprotonates a new molecule of Don-H with regeneration of Don^-. The base can be generated electrochemically using as probase the acceptor itself[4] or an auxiliary substance like azobenzene.[5] The base only needs to be present in very small amounts and accordingly the process requires only a catalytic quantity of electricity.

A similar mechanism has been recently postulated in the case of the addition of indene (InH_2) or fluorene (FlH_2) to nitrosobenzene;[6,7] the base corresponds to the anion radical of nitrosobenzene $ArNO^{\bullet-}$, which is protonated by the proton donor AH_2 (InH_2 or FlH_2) to give AH^-. Addition of AH^- to nitrosobenzene yields the anionic derivative $Ar(NO)(AH)^-$, which is also protonated by AH_2 to complete the cycle. Finally, Ar(NOH)(AH) is converted to the corresponding imine by dehydration at low temperature.

More recently, we have found that the same mechanism was involved with an aromatic aldehyde instead of nitrosobenzene.[8–10] Three consecutive chain reactions occur under the influence of the electrogenerated base $ArCHO^{\bullet-}$. The first step is the formation of the corresponding carbinol ArCH(OH)(AH) (AH = FlH or InH), the second the formation of ArCH=A and the third the addition of FlH_2 or InH_2 to the latter to give $ArCH(AH)_2$. There is much interest in finding new synthetic routes to the latter bis(indenyl) or bis(fluorenyl) methanes since they may serve as starting ligands to prepare the corresponding *ansa*-metallocenes.[11] The alkenyl products (ArCH=A), which can be regarded as substituted fulvenes, can themselves be used in the synthesis of the bridged metallocenes.[12] In recent years the main focus has been directed towards such complexes in the Group 4 series due to their polymerization catalytic properties.[13,14]

It must be noted that InH_2 or FlH_2 can add to aldehydes in the presence of a basic catalyst (potassium hydroxide,[15,16] sodium hydroxide,[17,18] $KF–Al_2O_6$ [19] or benzyltrimethyl hydroxide-triton B [4]). Nevertheless, the studies have been

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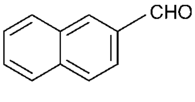
limited to a few aldehydes only. Moreover, the yields were found to depend on the kind of base as well as its ratio. By using the electrochemical method the quantity of catalyst is limited to what is needed to complete the reaction since the initiator is generated from controlled potential electrolysis of the aldehydic reactives.[10] In addition, some kinetic and mechanistic information can be obtained from the quantity of electrocatalyst, which is itself directly related to the charge consumed.

All these reasons prompted us to try to evaluate the scope of the electroinduced reaction for the synthesis of $\mathrm{ArCH(AH)_2}$ and we present in this paper the results of a study on the electrochemical reduction of 2-naphthaldehyde (**1**), 4-dimethylaminobenzaldehyde (**2**), 3-methoxybenzaldehyde (**3**) and 2-pyrrole carboxaldehyde (**4**) in the presence of fluorene ($\mathrm{FlH_2}$) or indene ($\mathrm{InH_2}$). The reaction is found to be selective: the additional organic function in **2**, **3** and **4** is not affected by the chain process.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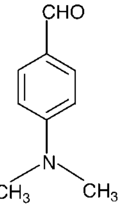
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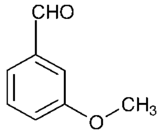
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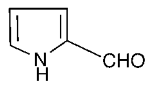
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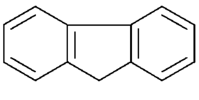
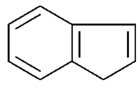

$\mathrm{FlH_2}$


$\mathrm{InH_2}$

Results and discussion

Electrochemistry and reaction mechanisms

Fig. 1, curve a, shows the cyclic voltammogram of naphthaldehyde in DMF–0.2 M n-$\mathrm{Bu_4NPF_6}$ at room temperature. Reduction peak A is observed in the cathodic sweep ($E_p =$ -1.8 V *vs.* SCE). If the potential is reversed after peak A, three oxidation peaks are found: peak A′ ($E_p = -1.70$ V), peak $\mathrm{A'_2}$ ($E_p = -0.5$ V) and peak $\mathrm{A'_3}$ ($E_p = -0.15$ V). Peak A corresponds to the reduction of **1** to its anion radical and peak A′ to the oxidation of this anion radical. Peaks $\mathrm{A'_2}$ and $\mathrm{A'_3}$ can be reasonably attributed to the oxidation of $\mathrm{(NpCHO)_2{}^{2-}}$ (Np = 2-naphthyl), which is obtained from dimerization of $\mathrm{NpCHO^{\bullet -}}$.[20]

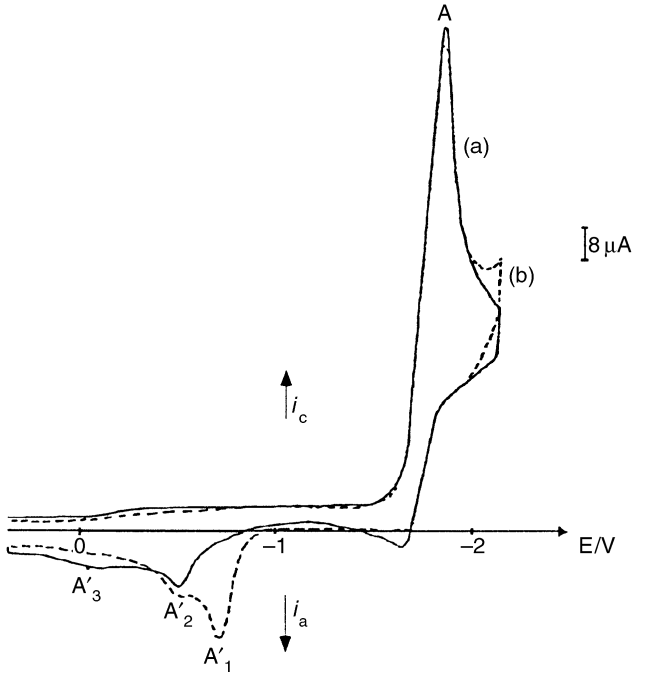


Fig. 1 Cyclic voltammogram of **1** in DMF–$\mathrm{Bu_4NPF_6}$ at room temperature: sweep rate 0.1 V $\mathrm{s^{-1}}$, starting potential +0.4 V. (*a*) **1** alone. (*b*) In the presence of 10 equiv. of $\mathrm{FlH_2}$.

In the presence of 10 equiv. of $\mathrm{FlH_2}$ (Fig. 1, curve b), peak A is not modified, oxidation peaks A′ and $\mathrm{A'_3}$ disappear and a new oxidation peak $\mathrm{A'_1}$ ($E_p = -0.72$ V) appears. The latter corresponds to the oxidation of the conjugate base $\mathrm{FlH^-}$, which is formed from deprotonation of $\mathrm{FlH_2}$ by either $\mathrm{NpCHO^{\bullet -}}$ or $\mathrm{(NpCHO)_2{}^{2-}}$. On the other hand, at low temperature (−20 °C) and in the presence of 10 equiv. of $\mathrm{FlH_2}$ (Fig. 2), peak A decreases and has a different shape (more rapid drop of current after reaching the peak potential). This is characteristic of a catalytic reaction occurring out of the diffusion layer,[7] a reaction that may be described as follows:

$$\underset{\mathbf{1}}{\mathrm{NpCHO}} + \mathrm{e^-} \rightarrow \mathrm{NpCHO^{\bullet -}} \qquad (1)$$

$$\mathrm{NpCHO^{\bullet -}} + \mathrm{FlH_2} \rightarrow \mathrm{NpCHOH^{\bullet}} + \mathrm{FlH^-} \qquad (2)$$

$\mathrm{NpCHO^{\bullet -}}$ produced in reaction (1) is protonated by $\mathrm{FlH_2}$, forming anion $\mathrm{FlH^-}$ and neutral radical $\mathrm{NpCHOH^{\bullet}}$. Alternatively, the dianionic dimer $\mathrm{(NpCHO)_2{}^{2-}}$ may also deprotonate $\mathrm{FlH_2}$. $\mathrm{FlH^-}$ diffuses towards the bulk of the solution and comes in contact with ArCHO, which moves to the electrode where reaction (3) takes place:

$$\mathrm{NpCHO} + \mathrm{FlH^-} \rightleftharpoons \mathrm{NpCHO(FlH)^-} \qquad (3)$$

Interestingly, such a chain reaction does not occur at room temperature, at least on the time scale of the cyclic voltammetry, since the intensity of peak A is unmodified by adding $\mathrm{FlH_2}$: reaction (3) must be slower. It has long been demonstrated[15] that temperature has a determining influence on this type of reaction: raising the temperature shifts equilibrium (3) to the left.

The chain reaction also does not occur on the coulometry time scale. Indeed, at room temperature, under the same conditions as the voltammetric studies, the current dropped to zero after the consumption of one electron per molecule of **1**. This is in contrast with the electroreduction of benzaldehyde, 2,6-dichlorobenzaldehyde and terephthalaldehyde in the presence of fluorene or indene for which the consumption of electricity was catalytic (10^{-3} to 10^{-2} equiv. of electrons per molecule of aromatic aldehyde).[9,10] Thus, the addition of

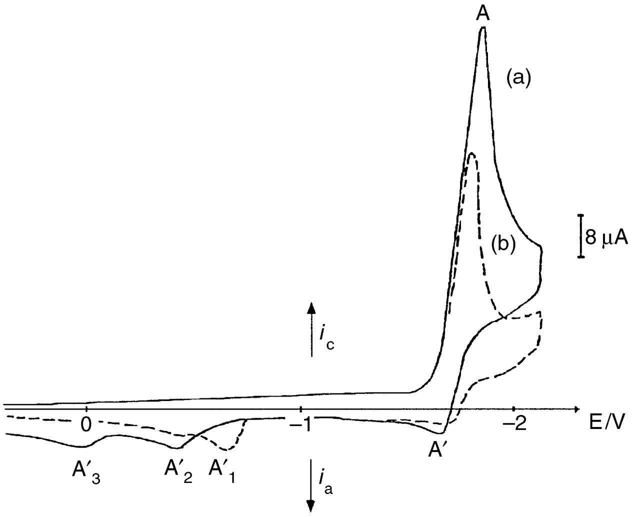


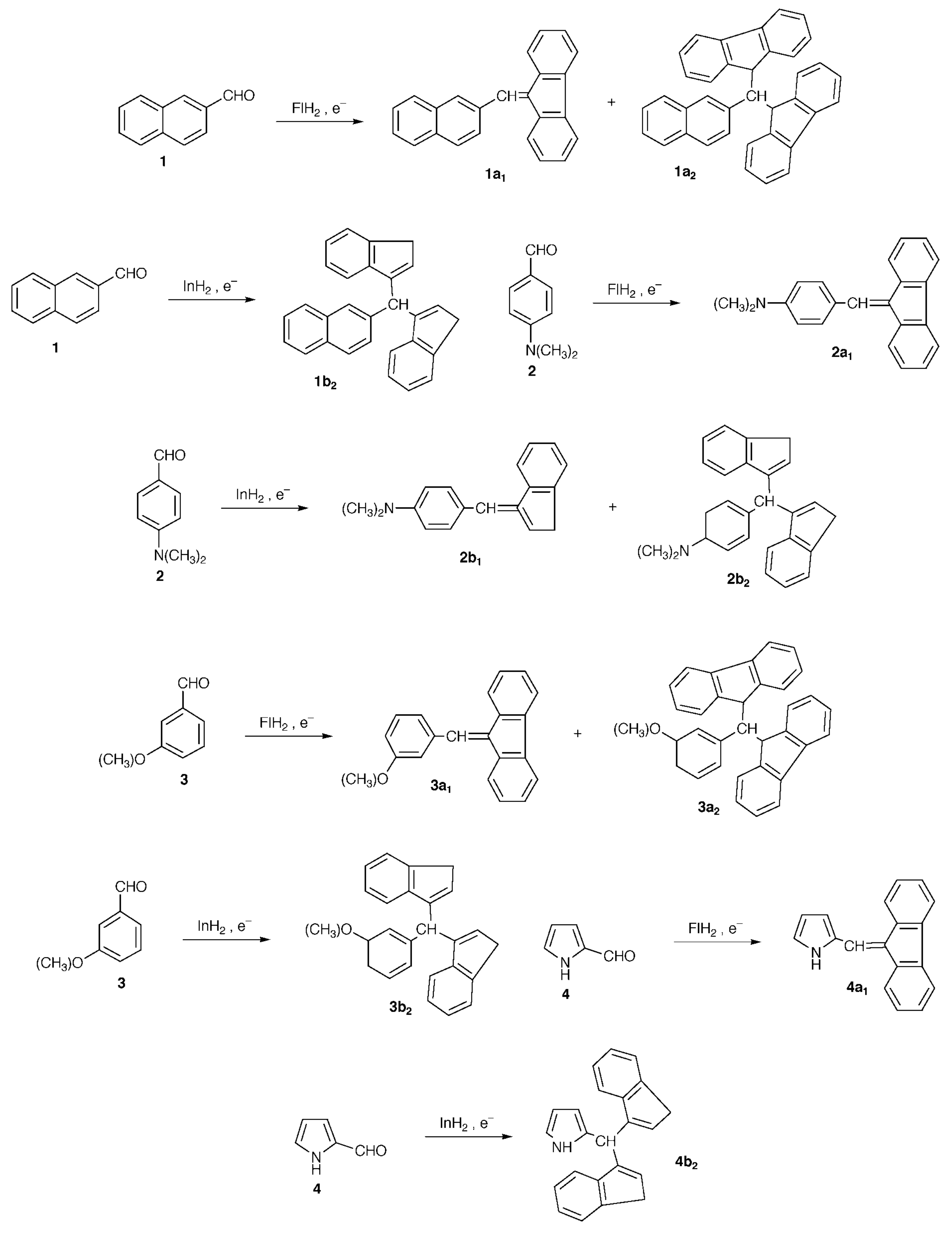
Fig. 2 Cyclic voltammogram of **1** in DMF–$\mathrm{Bu_4NPF_6}$ at −20 °C: sweep rate 0.1 V $\mathrm{s^{-1}}$, starting potential +0.4 V. (*a*) **1** alone. (*b*) In the presence of 10 equiv. of $\mathrm{FlH_2}$.

FlH^- to naphthaldehyde must be much slower than its addition to the previously studied benzaldehydes and terephthalaldehyde. In contrast, when the electrolysis of **1** in the presence of excess FlH_2 was performed as described above, except that it was stopped after a charge corresponding to 2.8×10^{-2} equiv. of electrons per mol of **1** had been consumed and the electrolysis solution was then kept at room temperature under argon for 70 h, products $\mathbf{1a_1}$ [9-(2-naphthylmethylene)-9*H*-fluorene] and $\mathbf{1a_2}$ {9-[9*H*-9-fluorenyl(2-naphthyl)methyl]-9*H*-fluorene} (see Scheme 1) were isolated in 17% and 41% yield, respectively (Table 1, entry 1), and identified by ^1H NMR spectroscopy, mass spectrometry and microanalysis. The formation of $\mathbf{1a_1}$ can be explained by equilibrium (3) followed by reaction (4) and (5):

$$NpCHO(FlH)^- + FlH_2 \rightarrow NpCH(OH)(FlH) + FlH^- \quad (4)$$

$$NpCH(OH)(FlH) \rightarrow \underset{\mathbf{1a_1}}{NpCH{=}Fl} + H_2O \quad (5)$$

Reaction (5) consists in the dehydration of the intermediate carbinol NpCH(OH)FlH under the influence of FlH^-, as we have previously mentioned.[10]



Scheme 1

Table 1 Controlled potential electrolysis of ArCHO in the presence of $\mathrm{FlH_2}$ or $\mathrm{InH_2}$ on a mercury electrode in DMF–n-$\mathrm{Bu_4NPF_6}$ (0.2 M) at room temperature followed by a variable standing time

Entry	ArCHO	$-E_w{}^a$ /V	$\mathrm{AH_2}$	Molar ratio $\mathrm{AH_2}$/ArCHO	Mol $\mathrm{e^-}$/mol ArCHO ($\times 10^2$)	Solution color	Standing time/h	Product(s) (% yield) ArCH=A	ArCH$\mathrm{(AH)_2}$
1	**1**	1.8	$\mathrm{FlH_2}$	15	2.8^b	Green	70	$\mathbf{1a_1}$(17)	$\mathbf{1a_2}$(41)
2	**1**	1.8	$\mathrm{InH_2}$	10	4.2^c	Grey	23		$\mathbf{1b_2}$(50)
3	**2**	1.95	$\mathrm{FlH_2}$	10	8^b	Red	23	$\mathbf{2a_1}$(50)	
4	**2**	2.15	$\mathrm{InH_2}$	10	26^c	Green	20	$\mathbf{2b_1}$(3)	$\mathbf{2b_2}$(34)
5	**3**	1.85	$\mathrm{FlH_2}$	4	10^b	Blue	24	$\mathbf{3a_1}$(33)	$\mathbf{3a_2}$(39)
6	**3**	1.85	$\mathrm{InH_2}$	8	10^b	Purple	20		$\mathbf{3b_2}$(45)
7	**4**	1.9	$\mathrm{FlH_2}$	10	5^b	Green	48	$\mathbf{4a_1}$(32)	
8	**4**	1.9	$\mathrm{InH_2}$	10	5^b	Purple	72		$\mathbf{4b_2}$(72)

^{a} Working potential *vs.* SCE. ^{b} Quantity of electricity imposed. ^{c} Quantity of electricity consumed by the time current had dropped to zero.

NpCH=Fl is a highly conjugated π-electron system so that it is electrophilic enough to react with excess $\mathrm{FlH_2}$ in a base-catalyzed process:

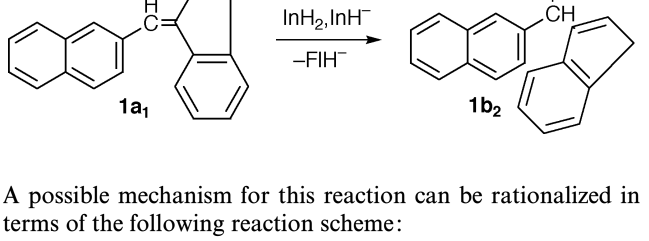
$$\mathrm{NpCH{=}Fl} + \mathrm{FlH_2} \rightleftharpoons \underset{\mathbf{1a_2}}{\mathrm{NpCH(FlH)_2}} \tag{6}$$

The first step is the addition of $\mathrm{FlH^-}$ to $\mathbf{1a_1}$, followed by proton transfer from $\mathrm{FlH_2}$ to the resulting anionic adduct and release of $\mathrm{FlH^-}$, which is able to react again. With the aim to demonstrate the occurrence of reaction (6), compound $\mathbf{1a_1}$ was reacted with a mixture of $\mathrm{FlH_2}$ and $\mathrm{FlH^-}$: $\mathbf{1a_2}$ was obtained in quantitative yield.

As outlined above the overall process is rather slow compared with earlier studied aldehydes so that at least one of the propagation steps [reactions(1)–(6)] must be slower. We believe that the slower steps are the addition of $\mathrm{FlH^-}$ to **1** and to $\mathbf{1a_1}$ (NpCH=Fl) and not the base-catalyzed dehydration of the carbinol. We already pointed out that the addition of $\mathrm{FlH^-}$ to **1** is slower than the addition to benzaldehyde and terephthalaldehyde.[10] But the slowest step, for steric reasons, must be the addition of $\mathrm{FlH^-}$ to $\mathbf{1a_1}$.

These two addition steps proved to be faster with $\mathrm{InH^-}$, which is less bulky than $\mathrm{FlH^-}$, as the nucleophile. Indeed, when replacing $\mathrm{FlH_2}$ by $\mathrm{InH_2}$ (entry 2 of Table 1), the current dropped to zero after the consumption of a catalytic quantity of electricity (4.2×10^{-2} equiv. of electron per mol of **1**), which shows that the addition of $\mathrm{InH^-}$ to **1** is faster than the corresponding addition of $\mathrm{FlH^-}$. The addition of $\mathrm{InH^-}$ on the alkenyl intermediate NpCH=In [2-(1*H*-3-indenylmethyl)naphthalene] is also faster than the addition of $\mathrm{FlH^-}$ to $\mathbf{1a_1}$. As evidence we did not succeed in isolating this intermediate, owing to its short lifetime. The bis(indenyl) adduct $\mathbf{1b_2}$ was obtained in 50% yield.

$\mathbf{1b_2}$ can also be obtained from $\mathbf{1a_1}$ in the presence of a mixture of $\mathrm{InH^-}$ and $\mathrm{InH_2}$ according to the global reaction:



A possible mechanism for this reaction can be rationalized in terms of the following reaction scheme:

$$\underset{\mathbf{1a_1}}{\mathrm{NpCH{=}Fl}} + \mathrm{InH^-} \rightleftharpoons \mathrm{NpCH(Fl)(InH)^-} \tag{7}$$

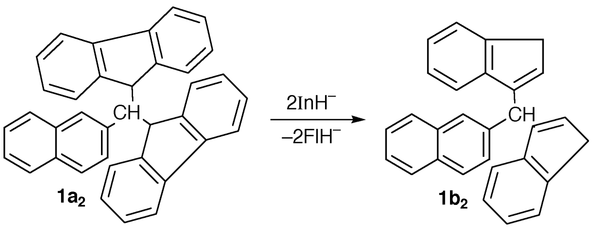
$$\mathrm{NpCH(Fl)(InH)^-} \xrightleftharpoons{\text{proton transfer}} \mathrm{NpCH(FlH)(In)^-} \tag{8}$$

$$\mathrm{NpCH(FlH)(In)^-} \rightleftharpoons \underset{\mathbf{1b_1}}{\mathrm{NpCH{=}In}} + \mathrm{FlH^-} \tag{9}$$

$$\mathrm{NpCH{=}In} + \mathrm{InH_2} \longrightarrow \underset{\mathbf{1b_2}}{\mathrm{NpCH(InH)_2}} \tag{10}$$

The first step consists in the nucleophilic addition of $\mathrm{InH^-}$ to $\mathbf{1a_1}$ to give the anionic intermediate $\mathrm{NpCH(Fl)(InH)^-}$ that, after an intramolecular proton transfer, eliminates $\mathrm{FlH^-}$ to give $\mathbf{1b_1}$, which immediately reacts with $\mathrm{InH_2}$ to yield $\mathbf{1b_2}$.

In addition, we have found that $\mathbf{1a_2}$ reacts easily with $\mathrm{InH^-}$ to give $\mathbf{1b_2}$:



(11)

A mechanism can be postulated in which $\mathrm{InH^-}$ successively displaces the two fluorenyl moieties. This reaction involves two base-catalyzed elimination-addition sequences. The first elimination gives $\mathbf{1a_1}$ and $\mathrm{FlH_2}$ [reaction (12)]. Then $\mathrm{InH^-}$ adds to $\mathbf{1a_1}$ [reaction (7)]. The second sequence consists in reactions (8), (9) and (10).

$$\underset{\mathbf{1a_2}}{\mathrm{NpCH(FlH)_2}} \rightleftharpoons \underset{\mathbf{1a_1}}{\mathrm{NpCH{=}Fl}} + \mathrm{FlH_2} \tag{12}$$

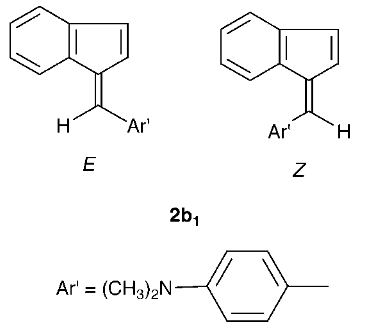
The cyclic voltammetric behavior of aldehydes **2**, **3** and **4** at room temperature is similar to that of naphthaldehyde **1**. There is no modification of the reduction peak A upon adding $\mathrm{FlH_2}$ or $\mathrm{InH_2}$, indicating that no chain reaction occurs on the voltammetric time scale at room temperature. The results of the electrolysis are given in Table 1, entries 3 to 8. The same types of products [ArCH=A and/or ArCH$\mathrm{(AH)_2}$] as those obtained with naphthaldehyde **1** were isolated. As in the case of the electrolysis of aldehyde **1** (entries 1 and 2), the reaction of $\mathrm{FlH^-}$ with ArCH=Fl is slower than the reaction of $\mathrm{InH^-}$ with ArCH=In. Indeed, with aldehyde **2**, only $\mathbf{2a_1}$ {*N*-[4-(9*H*-9-fluorenylidenemethyl)phenyl]-*N*,*N*-dimethylamine} (ArCH=Fl) was isolated after 23 h from the electrolysis in the presence of $\mathrm{FlH_2}$ whereas $\mathbf{2b_2}$ {*N*-[4-(di-1*H*-3-indenylmethyl) phenyl]-*N*,*N*-dimethylamine} [ArCH$\mathrm{(InH)_2}$] was the main product isolated after 20 h from the electrolysis in the presence of $\mathrm{InH_2}$. A similar observation can be made for the electrolyses of aldehyde **3** (compare entries 5 and 6) and of aldehyde **4** (compare entries 7 and 8).

Structure of products

To our knowledge all compounds are new compounds. They were characterized by ^{1}H NMR spectroscopy (Table 2), mass spectrometry (Table 3), microanalysis (Table 4) and infrared spectroscopy (Table 5).

Only one isomer of product $\mathbf{2b}_1$ {*N*-[4-(1*H*-1-indenylidene-methyl)phenyl]-*N*,*N*-dimethylamine} was isolated. We have been unable to determine, on the basis of the NMR spectroscopic data, if it was the *E* or *Z* isomer, but the *E* isomer should be more easily formed than the *Z* isomer since it is less hindered.

For product $\mathbf{1b}_2$ only one of the six most probable isomers shown in Scheme 2 has been isolated. Isomers $\mathbf{i}_1$ and $\mathbf{i}_3$ are interconvertible through two 1,5-sigmatropic rearrangements[21] or a base-catalyzed proton transfer[22,23] and isomers $\mathbf{i}_4$ and $\mathbf{i}_5$ through base-catalyzed transfers.



$\mathbf{2b}_1$

The same types of isomers can be drawn for $\mathbf{2b}_2$, $\mathbf{3b}_2$ {3-[1*H*-3-indenyl(3-methoxyphenyl)methyl]-1*H*-indene} and $\mathbf{4b}_2$ {2-(di-1*H*-3-indenylmethyl)-1*H*-pyrrole} but, as for $\mathbf{1b}_2$, only one product was formed.

The ^{1}H NMR spectra of all these compounds ($\mathbf{1b}_2$, $\mathbf{2b}_2$, $\mathbf{3b}_2$ and $\mathbf{4b}_2$) show that the indenyl moiety represented by InH

Table 2 ^{1}H NMR data

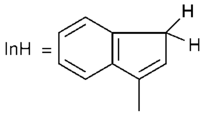
Product	δ	Multiplicity	Integration	*J*/Hz	Proton assignment
$\mathbf{1a}_1$	8.11	br s	1H	—	Olefinic
	7.05–7.96	[a]	15H	—	Aromatic
$\mathbf{1a}_2$	3.41–3.49	t	1H	7.9	ArC*H*(AH)$_2$
	5.12, 5.16	d	2H	7.9	ArCH(A*H*)$_2$
	6.84–7.79	m	—	—	Aromatic
$\mathbf{1b}_2$	3.53	br s	4H	—	Methylene
	5.70	br s	1H	—	ArC*H*(AH)$_2$
	6.21, 6.22	"d"	2H	1.5	Olefinic
	7.29–7.98	m	—	—	Aromatic
$\mathbf{2a}_1$	3.05	s	6H	—	Dimethylamino
	6.74–6.82	pert d	2H	8.9	*p*-Substituted benzene
	7.54–7.61	pert d	2H	8.9	*p*-Substituted benzene
	7.67	s	1H	—	Olefinic
	7.10–8.02	d and several m	—	—	Aromatic fluorene
$\mathbf{2b}_1$	3.03	s	6H	—	Dimethylamino
	6.70–6.97	pert d	2H	8.9	*p*-Substituted benzene
	7.55–7.62	pert d	2H	8.9	*p*-Substituted benzene
	7.43	s	1H	—	Olefinic
	6.97–7.71	dd and several m	—	—	Indenyl
$\mathbf{2b}_2$	3.12	s	6H	—	Dimethylamino
	3.59	br s	4H	—	Methylene
	5.55	br s	1H	—	ArC*H*(AH)$_2$
	6.29, 6.30	"d"	2H	1.3	Olefinic
	6.92–6.96	pert d	2H	8.9	*p*-Substituted benzene
	7.40–7.72	two m	—	—	Aromatic
$\mathbf{3a}_1$	3.84	s	3H	—	Methoxy
	7.68	s	1H	—	Olefinic
	6.93–7.81	two m	—	—	Aromatic
$\mathbf{3a}_2$	3.19–3.27	t	1H	7.9	ArC*H*(AH)$_2$
	3.37	s	3H	—	Methoxy
	4.99, 5.03	d	2H	7.9	ArCH(A*H*)$_2$
	6.21–7.77	[a]	—	—	Aromatic
$\mathbf{3b}_2$	3.43	br s	4H	—	Methylene
	3.81	s	3H	—	Methoxy
	5.40	br s	1H	—	ArC*H*(AH)$_2$
	6.11, 6.12	pert d	2H	1.6	Olefinic
	6.83–7.53	m	—		Aromatic
$\mathbf{4a}_1$	6.39–6.43	sex	1H	2.6	Pyrrolic
	6.73–6.77	pert s	1H	—	Pyrrolic
	6.90–6.94	sex	1H	2.7, 1.3	Pyrrolic
	7.24–7.81	two m	—	—	Aromatic
	8.19, 8.23	pert d	1H	7.3	
	8.47	very br s	1H	—	N*H*
$\mathbf{4b}_2$	3.42	br s	4H	—	Methylene
	5.49	br s	1H	—	ArC*H*(AH)$_2$
	6.11–6.14	pert s	1H	—	Pyrrolic
	6.18–6.24	m	3H	—	Olefinic and one pyrrolic
	6.68–6.71	sex	1H	2.9, 1.6	Pyrrolic
	7.19–7.53	two m	—	—	Aromatic
	8.04	very br s	1H	—	N*H*

[a] Several different multiplicities (m, t, dd, . . .).

Table 3 Mass spectral data

	m/z (% rel int)		
Product	Molecular ion	Other peaks	
1a$_1$	304(100)	165(2.2) FlH	—
1a$_2$	470(38.8)	305(100) −FlH	165(52.5) FlH
1b$_2$	370(100)	255(72.1) −InH	115(8.2) InH
2a$_1$	297(100)	252(16.4) $-NH(CH_3)_2$	—
2b$_1$	247(100)	202(25.4) $-NH(CH_3)_2$	—
2b$_2$	363(100)	248(54.1) −InH	203(13.9) $-InH - NH(CH_3)_2$
3a$_1$	284(100)	253(40.2) $-OCH_3$	
3a$_2$	450(20.3)	285(100) −FlH	165(14.5) FlH
3b$_2$	350(100)	235(57.4) −InH	115(12.3) InH
4a$_1$	243(100)	176(5) $-C_4H_5N$	163(7.2) $-C_5H_6N$
4b$_2$	309(100)	242(16.5) $-C_4H_5N$	194(58.2) −InH

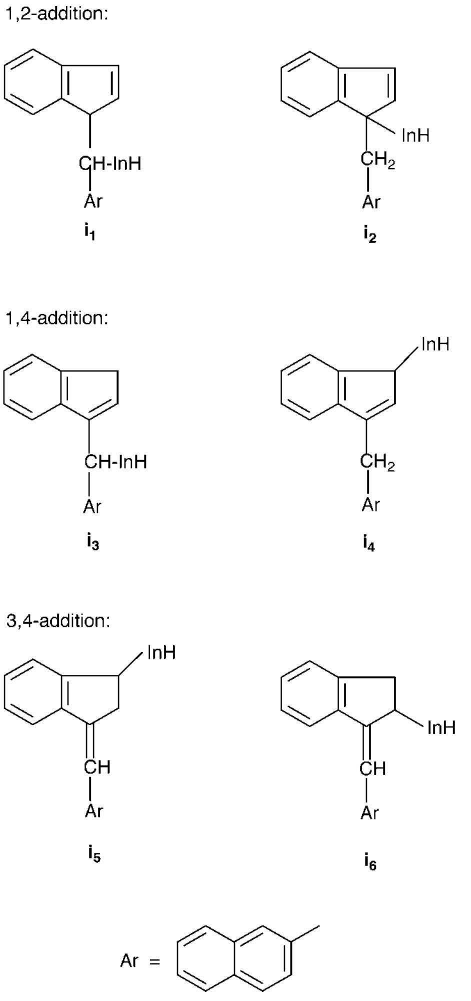
exists in a form where the double bond is trisubstituted (γ-form) since a four-proton singlet in the 3.42–3.59 ppm range appears in all spectra and only structure **i**$_3$ is in agreement with the ^{1}H NMR data.



γ-form

In the mass spectra (Table 3) the molecular ion peak was observed for all derivatives.

Compound **3a**$_1$ {9-[3-methoxyphenyl)methylene]-9*H*-fluorene} was reported to be crystalline in the literature (mp 145–146 °C[24]). However, it was obtained as an oil and has been fully characterized by elemental microanalysis, ^{1}H NMR spectroscopy and mass spectrometry.



Scheme 2

Table 4 Eluents for chromatographic separation, solvents for recrystallization, melting points and microanalytical data

					Microanalytical data					
					C/%		H/%		N/%	
Product	Chromatography eluent[a]	Recrystallization solvent	Melting point/°C	Molecular formula	Calcd	Found	Calcd	Found	Calcd	Found
1a$_1$	1 : 4	Hexane	98	$C_{24}H_{16}$	94.70	94.35	5.30	5.36		
1a$_2$	1 : 4	Hexane–CH_2Cl_2	229	$C_{37}H_{26}$	94.43	94.19	5.57	6.07		
1b$_2$	1 : 4	Hexane–CH_2Cl_2	152	$C_{29}H_{22}$	94.01	93.89	5.99	6.00		
2a$_1$	1 : 3	Hexane–CH_2Cl_2	132	$C_{22}H_{19}N$	88.85	88.83	6.44	6.36	4.71	4.68
2b$_1$	1 : 1	Hexane–CH_2Cl_2	158	$C_{18}H_{17}N$	87.41	87.02	6.93	6.89	5.66	5.47
2b$_2$	1 : 1	Hexane–CH_2Cl_2	154	$C_{27}H_{25}N$	89.21	88.41	6.93	6.97	3.86	3.60
3a$_1$	1 : 4		Oil[b]	$C_{21}H_{16}O$	88.73	88.46	5.63	5.66		
3a$_2$	1 : 4	Hexane–CH_2Cl_2	205	$C_{34}H_{26}O$	90.63	90.66	5.81	5.82		
3b$_2$	1 : 3	C_2H_5OH–H_2O	52–54	$C_{26}H_{22}O$	89.11	88.74	6.33	6.37		
4a$_1$	2 : 1	Hexane–CH_2Cl_2	94	$C_{18}H_{13}N$	88.86	88.77	5.38	5.48	5.76	5.76
4b$_2$	1 : 1	Hexane–CH_2Cl_2	101	$C_{23}H_{19}N$	89.28	89.10	6.19	6.38	4.53	4.22

[a] CH_2Cl_2–hexane. [b] Reported as crystalline in ref. 24.

Table 5 Assignment of characteristic bands in the IR spectra of compounds **1a**$_1$ to **4b**$_2$

Product	ν/cm^{-1}	Intensity	Assignment
1a$_1$	3013	m	Olefinic C–H stretch
1a$_2$	2892	w	Aliphatic C–H stretch
1b$_2$	2891	w	Aliphatic C–H stretch
2a$_1$	2805	m	N–CH_3, C–H stretch
2b$_1$	2814	w	N–CH_3, C–H stretch
2b$_2$	2805	m	N–CH_3, C–H stretch
3a$_1$	2832	m	O–CH_3, C–H stretch
3a$_2$	2832	m	O–CH_3, C–H stretch
3b$_2$	2833	m	O–CH_3, C–H stretch
4a$_1$	3406	s (sharp)	N–H stretch
4b$_2$	3419	s (sharp)	N–H stretch

Experimental

The apparatus and techniques used have been described previously.[10] ^{1}H NMR spectra were taken on a Bruker 200 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in δ downfield from internal tetramethylsilane. Infrared data were obtained on a Nicolet 205 spectrophotometer in the solid state using KBr as matrix.

2-Naphthaldehyde (**1**), 4-dimethylaminobenzadehyde (**2**) and 3-methoxybenzaldehyde (**3**) were commercially available. 2-Pyrrole carboxaldehyde (**4**) was synthesized according to a literature procedure.[25]

Typical electrolysis procedure

p-Dimethylaminobenzaldehyde **2** (608 mg, 4.08 mmol) was electrolyzed on a mercury electrode at -2.15 V *vs.* SCE with indene (5.1 ml, 43.6 mmol) in DMF (30 ml) containing *n*-Bu_4NPF_6 (0.2 M) at room temperature (see Table 1, entry 3). The electrolysis was stopped when the current dropped to zero (0.26 electrons per molecule of **2**). The electrolyzed solution was stirred for 20 h (the color turned from red to green) then poured into water and extracted with dichloromethane.

Chromatography on silica gel with hexane–dichloromethane (1 : 1) as eluent gave two products **2b**$_1$ (less polar) and **2b**$_2$ in 3% and 34% yield, respectively. Compounds **2b**$_1$ and **2b**$_2$ were characterized by ^{1}H NMR spectroscopy (Table 2), mass spectrometry (Table 3), elemental microanalysis (Table 4) and IR spectroscopy (Table 5).

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