

Solvent Catalysis, Mechanisms of Degenerate Metallation and Solvation of Ferrocenophanylpotassium and Ferrocenophanylsodium Studied by UV and NMR Spectroscopy

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Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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[1.1]Ferrocenophanylsodium **2** and [1.1]ferrocenophanylpotassium **3** undergo fast degenerate rearrangements in ethereal solvents which involve intramolecular 1,12-proton transfers coupled with 1,12-metal cation transfers as shown by NMR spectroscopy. The rearrangements of compounds **2** and **3** in diethyl ether (DEE) are catalyzed by tetrahydrofuran (THF). The catalysis is weaker for **3** than for **2**. The solvent-catalyzed reaction of **2** is first order with respect to THF at low THF concentrations showing that the activated complex contains one THF molecule more than the initial complex. The rearrangement of compound **3** in DEE is also catalyzed by small amounts of THF but in this case saturation kinetics are observed. The results show that when [THF] is increased the fraction of the initial state complexes containing one THF molecule also increases and that an activated complex for the catalyzed pathway contains one molecule of THF. Both the initial and activated complexes are found to be ion pairs. The solvent and temperature dependence of the nature of the initial complexes of **2** and **3** have been studied by UV-VIS spectroscopy. The sodium salt **2** appears to be mainly contact ion pairs over the whole temperature interval, ca. 17 °C to ca. –117 °C in DEE, 2-MTHF, 2,2-DMTHF and 2,5-DMTHF. In THF, on the other hand, compound **2** comprises contact ion pairs at room temperature and mainly solvent-separated or solvent-shared ion pairs at low temperatures. The potassium salt **3** is found to be contact ion pairs in all solvents used at all temperatures.

Despite the enormous applicability of organolithium and other alkali organometallic compounds in e.g. synthesis much remains to be known about the reaction mechanisms and in particular the roles of the cation and solvation.¹ Recently, we reported on the structure and solvation of [1.1]ferrocenophanyllithium (**1**) and the detailed mechanism and solvent catalysis of its degenerate lithiation reaction.^{2,3} We now report our results of UV-VIS studies of the ion pair nature of [1.1]ferrocenophanylsodium (**2**) and [1.1]ferrocenophanylpotassium (**3**), respectively in different ethereal solvents. Furthermore, results on the mechanism of solvent cata-

lysis of the degenerate rearrangement of **3**, which shows saturation kinetics, are presented.

Results and discussion

UV-VIS spectroscopy has been used to study ion pairing in solutions of **2** and **3**. Two broad bands, A and B, are observed for the solutions of the salts (Fig. 1). Band A is found in the 400–430 nm interval and band B in the 530–600 nm interval. These bands show alkali-cation, solvent and temperature dependence. Recently we reported that the UV spectrum of compound **1** in THF shows absorption maxima at 409 nm (band A) and 546 nm (band B) at 25 °C (Table 1). The ratio of the

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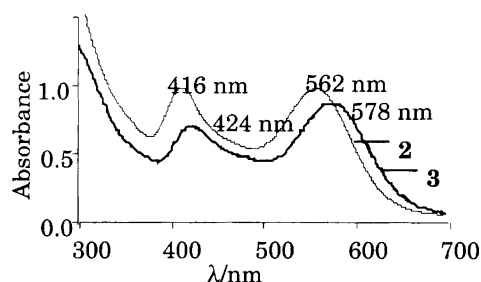


Fig. 1. UV-VIS spectra of **2** and **3** in THF at 17 °C and 22 °C.

absorbance of the two maxima, A_A/A_B , is 1.4. When the temperature was lowered to -100 °C, only small spectral changes were observed. The maxima shifted slightly to lower frequencies and the absorbance ratio diminished to 1.2. The color of the solution remained burgundy red all over the 125 °C interval.

Upon addition of a strong Li^+ complexing agent such as 12-crown-4, the spectral changes were substantial. There were pronounced red shifts of bands A and B by 15 nm and 33 nm, respectively. The absorbance ratio was inverted: $A_A/A_B = 0.9$ (at 23 °C), and the solution turned dark blue green. These results suggest that the addition of the crown ether separates the ions of a contact ion pair to yield a separated ion pair. The structure of these ion pairs remains to be clarified.

The spectrum of **1** in dimethoxyethane (DME) showed a dramatic temperature dependence. At 26 °C the spectrum was similar to that of **1** in THF (burgundy red solution): band A (411 nm), band B (552 nm), $A_A/A_B = 1.5$ (at 23 °C). When the temperature was lowered to -82 °C, there was a pronounced red shift similar to that observed upon addition of 12-crown-4 in THF. The shifts of the bands A and B were 19 nm and 36 nm, respectively. The absorbance ratio was inverted to 0.7, and the solution turned dark blue-green.

The effects of temperature and solvent are similar to those found by Hogen-Esch and Smid concerning the identification of solvent separated ion pairs (SSIPs) and contact ion pairs (CIPs).⁴ Our results suggested that when the temperature is lowered, the ion pair equilibrium shifts from mainly CIPs to more separated ion pairs that may be SSIPs or solvent-shared ion pairs in DME. An important note is that it is normally not possible to distinguish between SSIPs and free ions with this method.

The observed rate constant (k_{obs}) for the degenerate rearrangement of **1** has been measured in THF at different temperatures. A plot of $\log k_{\text{obs}}$ vs. $1/T$ is not curved, which indicates that there is no dramatic change of the initial state with temperature in this solvent. In DME on the other hand, the exchange is too fast on the NMR timescale to freeze out this process. It seems to be relatively faster at lower temperatures. This is consistent

Table 1. Collection of UV-VIS spectral data for **1-3** in some ethereal solvents together with assignments of the major type of ion pair.

Solvent/gegenion	$T/^\circ\text{C}$	A_A/nm	A_B/nm	$\Delta A/\text{nm}^a$	$\Delta B/\text{nm}^b$	A_A/A_B	Major type of ion pair
DEE/ Li^+	25	401	533			1.7	CIP
DEE/ Li^+	-116	403	537	+2	+4	1.5	CIP
THF/ Li^+	25	409	546			1.4	CIP
THF/ Li^+	-100	410	549	+1	+3	1.2	CIP
2,5-DMTHF/ Li^+	25	401	536			1.7	CIP
2,5-DMTHF/ Li^+	-114	405	538	+4	+2	1.4	CIP
DME/ Li^+	23	411	552			1.5	CIP
DME/ Li^+	-82	430	588	+19	+36	0.7	SIP
THF/12-crown-4/ Li^+	23	424	579			0.9	SIP
THF/12-crown-4/ Li^+	-100	429	585	+5	+6	0.7	SIP
DEE/ Na^+	17	411	553			1.2	CIP
DEE/ Na^+	-117	412	553	+0	+0	1.0	CIP
THF/ Na^+	17	416	562			1.0	CIP
THF/ Na^+	-117	430	590	+14	+28	0.6	SIP
2,5-DMTHF/ Na^+	22	414	554			1.7	CIP
2,5-DMTHF/ Na^+	-106	414	554	+0	+0	1.5	CIP
DEE/ K^+	18	418	568			0.9	CIP
DEE/ K^+	-96	418	568	+0	+0	0.9	CIP
THF/ K^+	22	424	578			0.8	CIP
THF/ K^+	-100	425	580	+1	+2	0.6	CIP
2,5-DMTHF/ K^+	18	418	569			1.2	CIP
2,5-DMTHF/ K^+	-114	418	569	+0	+0	0.9	CIP

^a $\Delta A = (A_{\text{max}}$ of Band A at low temperature) $- (A_{\text{max}}$ of Band A at high temperature) in the same solvent. ^b $\Delta B = (A_{\text{max}}$ of Band B at low temperature) $- (A_{\text{max}}$ of Band B at high temperature) in the same solvent.

with formation of more reactive ion pairs. The increased reactivity of **1** in DME in comparison with THF is probably due to the bidentate nature of DME.

UV spectra of the sodium salt (**2**) and the potassium salt (**3**) in THF at 17 °C and 22 °C, respectively are shown in Fig. 1. The absorption maxima of the two bands from **2** occur at 416 nm (band A) and 562 nm (band B) with a ratio of absorbance maxima equal to 1.0. The corresponding bands from **3** are found at 424 nm and 578 nm with an absorbance ratio of 0.81. Red shifts in absorption maxima upon increase of the cation radius ($r_{\text{Li}}=0.60 \text{ \AA}$; $r_{\text{Na}}=0.95 \text{ \AA}$ and $r_{\text{K}}=1.33 \text{ \AA}$) are expected since with an increase of the interionic distance the perturbation of the anion by the cation decreases, i.e. the charge localization in the anion decreases. Similar red shifts have earlier been shown to occur for a variety of anionic species upon increase of the radius of the cation.⁵

When the temperature of a THF solution of **2** was lowered from 17 °C to -117 °C the color changed from red to dark blue-green. Thus there were pronounced red shifts of bands A and B for **2** by 14 and 28 nm, respectively (Fig. 2 and Table 1).

The absorbance ratio A_A/A_B changed from 1.0 to 0.6. These results suggest that lowering of the temperature had led to increased distance between the ions in the ion pairs due to increased solvation by THF of the sodium ions and that the ion pair solution at -117 °C is composed of mainly SSIPs or solvent-shared ion pairs. These results contrast the behavior of compound **1**, a solution of which remained burgundy red even at -117 °C, and thus the ion pairs remained contact ion pairs throughout the temperature interval. Lowering of the temperature from 22 °C of a THF solution of **3**, which is dark blue, to -100 °C did not change the color of the solution. Bands A and B shifted only 1 nm and 2 nm, respectively. These results indicate that the ion pairs with potassium ions remain contact ion pairs throughout the temperature interval, like for the lithium salt **1**. The small band shifts measured at the lowest temperatures both for **1** and **3** might be due to the contribution of a small fraction of contact ion pairs with the cation solvated by an extra THF molecule.

The unexpected irregular behavior of the sodium salt

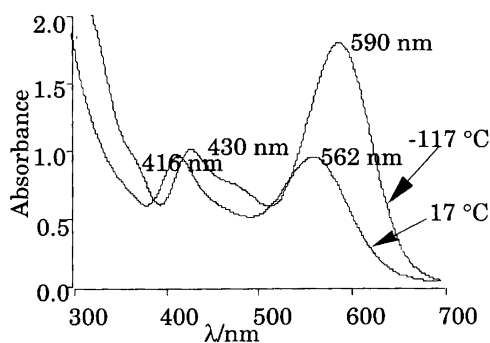


Fig. 2. UV-VIS spectra of **2** in THF at 17 °C and -117 °C.

2 might have the following explanation. For SSIPs or solvent-shared ion pairs to be dominant species in solution their standard free energy has to be lower than for the corresponding CIPs. Increasing the solvation of the cation causes both the enthalpy and entropy to be lowered. However, decreased entropy results in increased free energy and the magnitude of the free energy increase increases with the temperature T . In other words the entropy cost that has to be paid upon solvation increases with temperature. Furthermore, for the transition from CIPs to SSIPs or solvent-shared ion pairs to occur, the distances between the anions and their corresponding cations must be increased; this reduces the enthalpy but may be accompanied by some entropy increase.

In solution the initial state of **1** is presumably mainly made up of carbanion-lithium ion ion pairs with the lithium ion solvated by two ethereal solvent molecules, as in the solid state. Introduction of another solvent ligand onto the lithium ion results in increased free energy because of steric interactions due to crowding at the lithium ion. Obviously the lower entropy cost for coordinating a solvent molecule to the lithium ion at the lowest temperatures is not enough to compensate for the total enthalpy increase (this increase is the sum of enthalpy changes caused by separating the ions and ligating a solvent molecule). The sodium ion in compound **2** has a larger surface area than the lithium ion and therefore has space for more ligands. However, there are indications that the sodium ion may not be solvated by more THF molecules than the lithium ion at room temperature. A reason for this may be that with few ligating dipoles these have freedom to move on the surface of the ion and therefore the entropy loss accompanying their coordination is smaller than for lithium. Owing to the larger surface area available on the sodium ion than for the lithium ion the motion of a dipole becomes less restricted upon ligating a sodium ion compared with ligating a lithium ion. The entropy cost of binding an extra dipole to the sodium ion is therefore predicted to be smaller than for bonding to lithium ion. However, at room temperature the free energy change due to entropy ($-T\Delta S^\circ$) is larger than the decrease in enthalpy. Lowering of the temperature lowers the entropy cost and as a result initial complexes with increased sodium solvation become predominant at low temperatures, i.e. the species consists mainly of SSIPs or solvent-shared ion pairs.

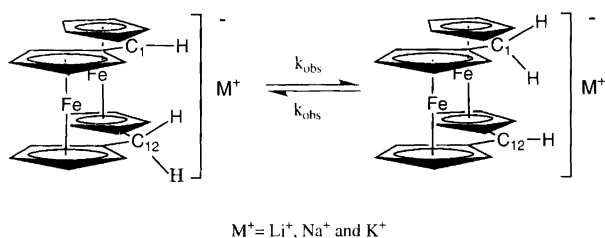
Similar reasoning could apply to the potassium salt **3** and it is concluded that at the lowest experimental temperature, -100 °C, the predominant species are still CIPs. However, SSIPs or solvent-shared ion pairs may become the major species at even lower temperatures.

It is interesting to note in Table 1 that in more sterically demanding solvents the ion pairs appear to be tighter (bands are blue-shifted) possibly because the fraction of ion pairs with less solvated cations is larger in such solvents. It is also interesting to note that lowering of the temperature in some cases yields an increased fraction

of ion pairs with more solvated cations (small red shifts of the bands). However, no detectable solvation change with temperature was found for the tight ion pairs of sodium salt **2** and potassium salt **3** in DEE and 2,5-DMTHF.

Solvent catalysis of the degenerate metallation. The degenerate metallation of compound **3** involves an intramolecular 1,12-proton transfer coupled with a 1,12-potassium ion transfer (Scheme 1). The rate of the rearrangement of **3** shows, like compounds **1** and **2**, strong solvent dependence, e.g. the rate is much faster in THF than in DEE (Table 2).

The potassium salt **3** is more reactive than **2** which in turn is more reactive than **1**. In DEE at $-53\text{ }^\circ\text{C}$ the rearrangement of **3** is slow on the NMR timescale and small additions of THF have been found to catalyze the rearrangement. The results are shown in Fig. 3 together with previously published results for **1** and **2**.^{2,3} The observed rate constants (k_{obs}) are plotted as a function of mol% THF in DEE. The catalysis of **3** is different from that of **1** and **2**. The rate of change of k_{obs} for **3** with mol% THF decreases with increased mol% THF. This levelling off indicates a saturation effect. Extrapolation suggests that k_{obs} becomes independent of mol% THF at high THF concentrations. These results suggest that upon addition of THF a new pathway for the rearrangement is opened. This pathway operates in parallel with the DEE pathway. The latter pathway has the activated complex containing x DEE molecules, and the former makes use of an activated complex in which a THF molecule coordinates with the potassium ion besides the x DEE molecules. No information regarding the value of x is at present available.



Scheme 1.

Table 2. Influence of alkali-metal cation and solvent on the degenerate 1,12-metallation in [1.1]ferrocenophanyl salts.

Alkali-metal cation	$T/^\circ\text{C}$	Solvent	$k_{\text{obs}}/\text{s}^{-1}$
Li^+	21	DEE	8.3
Li^+	21	THF	3.2×10^4
Li^+	-100	THF	63
Na^+	19	DEE	260
Na^+	-44	DEE	7.5
Na^+	15	THF	Fast ^a
Na^+	-85	THF	Fast ^a
K^+	-53	DEE	63

^aExchange too fast for a determination of k_{obs} .

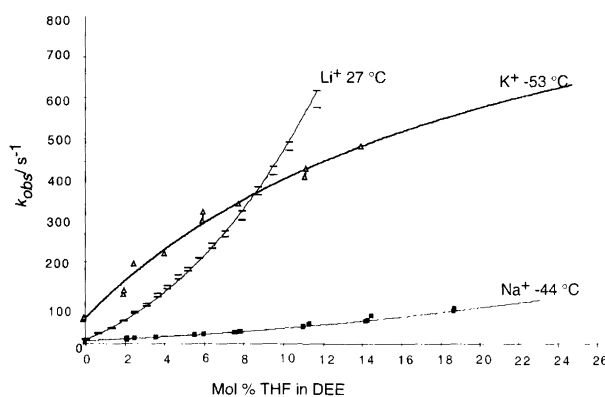
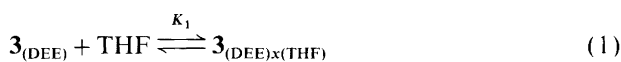


Fig. 3. The observed rate constants (k_{obs}) for the degenerate rearrangements of compounds **1–3** plotted against mol% THF in DEE. The curves for **1** and **2** have been simulated as described in Ref. 3. The curve for **3** has been simulated using eqn. (3).

In eqn. (1) the assumed equilibrium between the initial complexes in the rearrangement of **3** is shown.



In eqn. (2) the observed rate $k_{\text{obs}}[\mathbf{3}]_{\text{tot}}$ is expressed as the sum of the rate $k_1[\mathbf{3}_{(\text{DEE})x}]$ and the rate $k_2[\mathbf{3}_{(\text{DEE})x}]$.

$$k_{\text{obs}}[\mathbf{3}]_{\text{tot}} = k_1[\mathbf{3}_{(\text{DEE})x}] + k_2[\mathbf{3}_{(\text{DEE})x}][\text{THF}] \quad (2)$$

Using the following expression for the equilibrium in eqn (1), $K_1 = [\mathbf{3}_{(\text{DEE})x(\text{THF})}]/[\mathbf{3}_{(\text{DEE})x}][\text{THF}]$, and eqn. (2), eqn. (3) is obtained. In eqn. (3) k_{obs} is expressed as a function of k_1 , k_2 and $[\text{THF}]$.

$$k_{\text{obs}} = (k_1 + k_2[\text{THF}]) / (1 + K_1[\text{THF}]) \quad (3)$$

The rate constant k_1 was assumed to be identical with k_{obs} in pure DEE, i.e. 60 s^{-1} . The curve in Fig. 3 was obtained by simulation using $k_1 = 60\text{ s}^{-1}$ and the parameters $k_2 = 510\text{ M}^{-1}\text{ s}^{-1}$ and $K_1 = 0.5\text{ M}^{-1}$. The inaccuracy of the latter parameters is substantial.

In Fig. 4 a qualitative free energy diagram for the THF catalysis of **3** is constructed. The catalysis of **3** contrasts that of **1** and **2**, which did not show saturation kinetics (Fig. 3). At low concentrations of THF the catalysis of **1** and **2** is first order in THF and there is

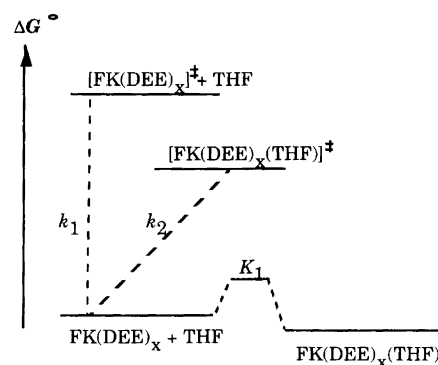


Fig. 4. Qualitative standard free energy diagram for the solvent-catalyzed metallation in **3**.

only transition-state stabilization by one THF molecule. There is no detectable evidence for initial-state stabilization by THF complexation. At higher THF concentrations pathways with activated complexes with more than one THF molecule become important and so does initial-state stabilization by THF (Fig. 3). The rate and equilibrium parameters in DEE for **3** at -53°C were $k_1 = 60\text{ s}^{-1}$, $k_2 = 510\text{ M}^{-1}\text{ s}^{-1}$ and $K_1 = 0.5\text{ M}^{-1}$. The related parameters for **1** at 27°C have previously been determined to be: $k_1 = 0.9\text{ M}^{-1}\text{ s}^{-1}$, $k_2 = 200\text{ M}^{-1}\text{ s}^{-1}$ and $K_1 = 1.0$. Those for compound **2** at -44°C are: $k_1 = 0.75\text{ M}^{-1}\text{ s}^{-1}$, $k_2 = 20\text{ M}^{-1}\text{ s}^{-1}$ and $K_1 = 1.0$. It should be remembered that K_1 for **3** and the K_1 for **1** and **2** have different dimensions. The equilibrium for **3** is an association equilibrium but those of **1** and **2** are exchange equilibria.

Experimental

General. All solvents were distilled in an inert atmosphere from sodium–benzophenone prior to use. The deuteriated solvents were stored over Deporex (Fluka AG) and distilled on a vacuum line and then stored in a Glovebox (Mecaplex GB-80 equipped with a gas-purification system that removes water and oxygen from the nitrogen atmosphere in the box). The water content inside the box was less than 2 ppm. All glass equipment and gas-tight syringes used in the experiments were assembled in the glove box. The edges of the syringe needles were protected with a septum when being transferred outside the glovebox.

Preparation of [1.1]ferrocenophanylpotassium (3). [1.1]Ferrocenophane, typically 3 mg ($7\text{ }\mu\text{mol}$), weighed on a balance inside the glovebox was added directly into an NMR tube (Wilma/Omnifit system, 507-OF). Usually $600\text{ }\mu\text{l}$ of $[\text{}^2\text{H}_{10}]\text{-DEE}$ were added and the NMR tube was sealed using a Wilma/Omnifit valve assembly (OFV). The solution was cooled to -70°C outside the glovebox and $20\text{ }\mu\text{l}$ of a 0.2 M slurry of CH_3K in hexane ($4\text{ }\mu\text{mol}$) was added by a gas-tight syringe. The fraction of **3** formed was monitored by ^1H NMR spectroscopy at -53°C . Successive additions of CH_3K gave solutions with the required composition. In between each addition the reaction mixture was cooled to -70°C . The preparation of CH_3K presented below is similar to earlier reported procedures.^{6,7} Potassium *tert*-butoxide (0.72 g, 6.4 mmol) was dissolved in 40 ml diethyl ether and the solution obtained was cooled in acetone–ice. A solution of methyl lithium in DEE 1.6 M (4.1 ml , 6.5 mmol) was added by means of a syringe and the mixture was stirred for 10 min during which time solid material was formed. After centrifugation the supernatant liquid was removed. The remaining solid material was washed three times with $3 \times 10\text{ ml}$ DEE and flushed with argon overnight. A slurry was made with hexane, which was used in the experiment above. In the catalysis experiment

$[[1.1]\text{ferrocenophane}] < [\mathbf{3}]$ and the concentration of **3** in $[\text{}^2\text{H}_{10}]\text{DEE}$ was ca. 9 mM .

Solvent catalysis. Mixtures of $[\text{}^2\text{H}_{10}]\text{DEE}$ and $[\text{}^2\text{H}_8]\text{THF}$ were prepared and used for additions of small amounts of $[\text{}^2\text{H}_8]\text{THF}$. NMR spectra were recorded after each addition. Rate constants were determined from band-shape analysis using the program DNMR 5. Reproducibility was demonstrated using three different samples which were investigated in parallel. Compound **3** was not recrystallized before used in the catalysis experiments but used directly after preparation.

NMR spectroscopy. The ^1H NMR spectral experiments were carried out on a Varian Unity 500 spectrometer operating at 499.92 MHz using standard parameters for ^1H . The low-temperature control system consisted of a long hold VT-liquid nitrogen Dewar with a heat exchanger, attached to a mixer for mixing cold and warm nitrogen. Temperatures in the probe were measured with a calibrated methanol thermometer supplied by Varian.

UV–VIS spectroscopy. The experiments were carried out on a Cary 04 spectrophotometer. The cuvettes were placed in an Oxford variable-temperature liquid nitrogen cryostat model DN1704 equipped with an ITC-4 temperature controller. The temperature was measured close to the cuvette with a S25421 thermolyzer (Systemteknik Lidingö, Sweden) equipped with a Pt 100:1/10 DIN temperature sensor. The cuvettes were from Helma (No. 220-QS, 1 mm width and 10 mm length) onto which the top of a Wilma/Omnifit system, 507-OF NMR tube was connected. The Wilma/Omnifit valve assembly (OFV) was used to close the cuvette. Compound **3** was prepared directly in the cuvette. Typically 1 mg of [1.1]ferrocenophane was weighed on a balance and placed in the cuvette inside the glovebox. About 1 ml of solvent was added. The cuvette was placed in an ice–acetone bath and typically $10\text{ }\mu\text{l}$ of slurries of either CH_3K (2.1 M) or CH_3Na (2.1 M) or a solution of BuLi (2.0 M) in hexane were added.

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