

The lithiation of ferrocene and ruthenocene: a retraction and an improvement¹

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Abstract

We reported in 1993 an efficient synthesis of ferrocene and ruthenocene mono- and dialdehydes which suggested the first truly specific monolithiation of these two metallocenes (U.T. Mueller-Westerhoff, Z. Yang and G. Ingram, *J. Organomet. Chem.*, 463 (1993) 163). Unfortunately, these results were based on inappropriate experimental methods. We have now meticulously analyzed a wide spread of reaction conditions and have concluded that an effective monolithiation of ferrocene and of ruthenocene is possible, but not under the previously described reaction conditions.

Keywords: Iron; Ruthenium; Lithium; Metallocenes; Aldehydes; Metalations; Lithiation

1. Introduction and background

It appears that a recent publication from this laboratory has been based in part on false information [1]. The other portions of that publication are reproducible and beyond doubt. What is in serious doubt are two reactions: (a) the selective monolithiation of ferrocene, leading (after addition of DMF) to ferrocene carboxaldehyde in 91% yield and (b) the equally successful (90.5% yield of the aldehyde) monolithiation of ruthenocene. We therefore want to retract these parts of the above publication.

Shortly after the above publication had appeared, we were notified by Professor H. Kagan that efforts to produce the ferrocene carboxaldehyde according to our procedure had produced quite different results: a mixture of unreacted ferrocene (45%), monoaldehyde (26%) and dialdehyde (16%) was obtained [2]. At that time, we believed that attention had to be paid to the reaction details, but the success of the two reactions was not in doubt. However, when repeated attempts in our labora-

tory to prepare ferrocene carboxaldehyde failed to produce more than a 60% yield, we decided to re-investigate the ruthenocene lithiation as well. The results were even more disturbing: unreacted ruthenocene was recovered, and the usual three lithioruthenocenes (mono-, di-, and trilithioruthenocene) were obtained in comparable amounts.

Meanwhile, Guillaneux and Kagan have published an efficient two-step method to obtain monolithioferrocene via the alkyl lithium cleavage of tributylstannylferrocene [3]. Although this, in principle, solves the monolithiation problem for ferrocene, we were interested in clean and simple one-step synthetic procedures for both ferrocene and ruthenocene, with a degree of efficiency similar to the one erroneously published by us.

A very careful and systematic re-examination of all reaction conditions and of product distributions under widely varying conditions has led us to conclude that:

1. there is a remote possibility that the monolithiation of ferrocene is possible under the published conditions, but these are nearly impossible to reproduce;
2. the clean monolithiation of ruthenocene does not occur under the published conditions;
3. competitive lithiation of ferrocene/ruthenocene mixtures clearly confirms the known higher reactivity of ruthenocene [4];
4. in spite of the higher reactivity of ruthenocene,

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¹ Taken in part from the M.S. Thesis of R. Sanders, University of Connecticut, 1995. Dedicated to Professor Marvin D. Rausch, a good friend (and one of the first persons to struggle with the metallation of ferrocene and ruthenocene) on the occasion of his 65th birthday.

which usually leads to multiple lithiations under all previously known reaction conditions including the one in our previous paper, there exists a set of reaction conditions under which a reasonably clean monolithiation can be achieved.

The following describes how the monolithiation of the two metallocenes was optimized. Two new reproducible procedures for the synthesis of ferrocene carboxaldehyde (90.7% yield) and ruthenocenaldehyde (80.9% yield) have resulted from this work.

2. Results and discussion

2.1. Ferrocene lithiations

Some of the obvious variables in the lithiation of ferrocene are: (1) the choice of lithiating reagent (*n*-BuLi, *s*-BuLi, *t*-BuLi); (2) the ratio of ferrocene to lithiating reagent; (3) the choice of solvent; (4) the reaction temperature; (5) the addition mode; (6) the rate of addition; (7) the concentration; (8) the reaction time. The effect of most of these is of a general nature and is well understood. However, especially in lithiation reactions of ferrocene, much contradictory information also exists. Some less obvious variables seem to play a role, as evidenced by variations in yield in different reactions run under seemingly identical conditions. It is this uncertainty which caused us to go to great lengths and much repetition before we could firmly state that the published procedure was indeed wrong.

In the over forty ferrocene lithiations we studied with the aim of producing a clean monolithiation, all of the above variables were investigated. The results are summarized in Table 1.

A few additional points can be made.

1. Ferrocene and *n*-BuLi do not react to any useful extent [5] unless the *n*-BuLi is activated by TMEDA

(*N,N,N',N'*-tetramethyl-1,2-diaminoethane) or other bases. Since the presence of TMEDA also favors dilithiation, *n*-BuLi is not useful in this reaction. The reaction of ferrocene with *s*-BuLi shows that it does react, but its intermediate reactivity offers little advantage over *t*-BuLi, which we therefore have used in the majority of reactions.

2. THF is the best choice of solvent, although its reactivity towards *t*-BuLi at temperatures above -20°C is a severely limiting factor.
3. The rate of addition of an alkane solution of *t*-BuLi to the THF solution of ferrocene is a significant variable: extremely slow addition favors monolithiation. This appears to be due to local heating effects, when the *t*-BuLi clusters in hexane or pentane are broken up in the solvation by THF. These temperature fluctuations lead to dilithiation.
4. Because lithioferrocene is less soluble than ferrocene, it precipitates from THF when too small amounts of solvent are used. In doing so, it may include and coprecipitate some ferrocene, which then escapes lithiation. The ferrocene remaining in solution is then more prone to double lithiation.
5. At low reaction temperatures, the reaction time has to be drastically extended to allow for complete conversion.

In spite of these in-depth studies, we have not found a single set of conditions which would allow us to reproducibly obtain monolithioferrocene in a one-step reaction from ferrocene and *t*-BuLi in yields above 75%. For this reason, we looked at the action of "super bases" and studied the lithiation of ferrocene by *t*-BuLi in the presence of KO*t*-Bu.

This led to the desired success only after some disappointing first results. When a 1:1:1 ratio of ferrocene:*t*-BuLi:KO*t*-Bu was used in a reaction at -74°C , the product distribution was similar to reactions at -20°C without added KO*t*-Bu: some *t*-BuLi was con-

Table 1
Some lithiations of ferrocene under varying conditions

RLi (type)	FcH/RLi (ratio)	KO <i>t</i> -Bu (vs. FcH)	Temp. ($^{\circ}\text{C}$)	Time (min)	FcH/Fc(CHO)/Fc(CHO) ₂ percentage of original FcH	Comments
<i>t</i> -BuLi	1:1.5	0	-20	30	5.0:91.0:1.0	Ref. [1]
<i>t</i> -BuLi	1:1.5	0	-20	30	57.0:28.0:15.0	Ref. [2]
<i>t</i> -BuLi	1:1.5	0	-20	30	50.0:29.0:20.0	
<i>s</i> -BuLi	1:1.6	0	-10	15	50.0:12.2:30.4	
<i>t</i> -BuLi	1:2.0	0	-20	190	66.2:14.8:24.8	
<i>t</i> -BuLi ^a	1:0.5	0.5 ^b	-74	60	—:90.4:8.0	
<i>t</i> -BuLi ^a	1:0.5	0.5 ^c	-74	60	—:60.6:23.4	
<i>t</i> -BuLi ^a	1:0.5	0.25 ^c	-74	60	—:60.1:7.6	
<i>t</i> -BuLi ^a	1:0.8	0.15 ^c	-74	60	—:64.8:2.8	
<i>t</i> -BuLi	1:1.5	0.125	-74	60	15.0:83.4:1.6	
<i>t</i> -BuLi	1:2.0	0.125	-74	60	11.0:86.0:2.7	
<i>t</i> -BuLi ^d	1:2.0	0.125	-74	60	4.0:90.7:4.9	

^a In reactions using excess FcH, the yield is based on *t*-BuLi. ^b Reaction using old KO*t*-Bu of dubious activity. ^c Reaction using active KO*t*-Bu.

^d Large scale reaction.

sumed by the solvent, and mono- and dilithiation was observed. This is not surprising in hindsight: the activated *t*-BuLi at -70°C is similar in its reactivity to unactivated *t*-BuLi at -20°C . It is possible to specifically lithiate ferrocene and to obtain very reproducibly the monoaldehyde in yields near 90%, based on ferrocene, if only a small amount of KO*t*-Bu is used to activate the *t*-BuLi. The reaction uses a twofold excess of *t*-BuLi, and is conducted at -74°C in the presence of 1/8 equiv. KO*t*-Bu. Details are given in the Experimental section. It appears that conducting the reaction at low temperature is of advantage in effecting the monolithiation. An excess of *t*-BuLi is necessary because some of it is consumed by the solvent when activated even only by a small amount of KO*t*-Bu and even at very low temperatures.

One additional reason to conduct the lithiation of ferrocene at low temperatures was our concern that a scrambling reaction might be involved, which in its simplest case would amount to a disproportionation of Fc-Li (Fc = ferrocenyl) to ferrocene and FcLi₂, which we expected to be able to suppress at lower temperature.



We tried to establish the presence or absence of such an equilibrium by transferring part of a lithiation reaction (1:1:1 ratio of FcH:*t*-BuLi:KO*t*-Bu, -70°C) and quenching it with DMF, adding more ferrocene to the rest, and quenching this reaction with DMF after a given reaction time. A comparison of the product distributions was expected to provide insight into this equilibrium question. Unfortunately, the results are inconclusive; although the FcLi/FcLi₂ ratio increases upon addition of ferrocene, the calculated equilibrium constants for the two reactions (7.1 and 1.6 respectively) are too different to allow us to consider this to be an equilibrium. Rather, the longer overall reaction time can be held responsible for more complete monolithiation.

A lithiation conducted at -20°C and without KO*t*-Bu again showed similar results: the two equilibrium con-

stants (1.37 and 2.60) were too different to allow a direct conclusion.

When the paper by Guillaneux and Kagan appeared [3], it became apparent that these authors had addressed similar concerns. They also saw a decrease in lithioferrocene through reaction with the solvent but no formation of dilithioferrocene.

2.2. Relative reactivity of ferrocene and ruthenocene towards *t*-BuLi

Although it has been established long ago by Rausch et al. [4] that ruthenocene is more reactive towards lithiation than ferrocene, our renewed doubts about conclusions derived from product distributions in reactions carried out under apparently identical conditions led us to look at the reactivity differences in a competitive lithiation. To this effect, a mixture of equimolar amounts of ferrocene and ruthenocene was treated in THF at -30°C with excess *t*-BuLi, and then converted to the aldehyde products by addition of DMF. After standard workup, the products were separated by column chromatography. Unreacted ferrocene was recovered in 60% yield, whereas only 26% of unreacted ruthenocene was recovered. The distribution of unreacted metallocenes [6] and of aldehyde products was also analyzed by GC-MS (Fig. 1) and showed a large predominance of ruthenocene carboxaldehyde, with the di- and trialdehydes present in much smaller amounts. Ferrocene carboxaldehyde was present in a significant amount, but the dialdehyde was barely detectable.

This result is in full accord with earlier experimental work as well as with theoretical results which assign much less negative charge to the Cp rings of ruthenocene than of ferrocene and thus predict a higher acidity of the ruthenocene system.

2.3. Lithiation of ruthenocene

An initial run attempting to repeat the published lithiation procedure [1] for ruthenocene (RcH) was re-

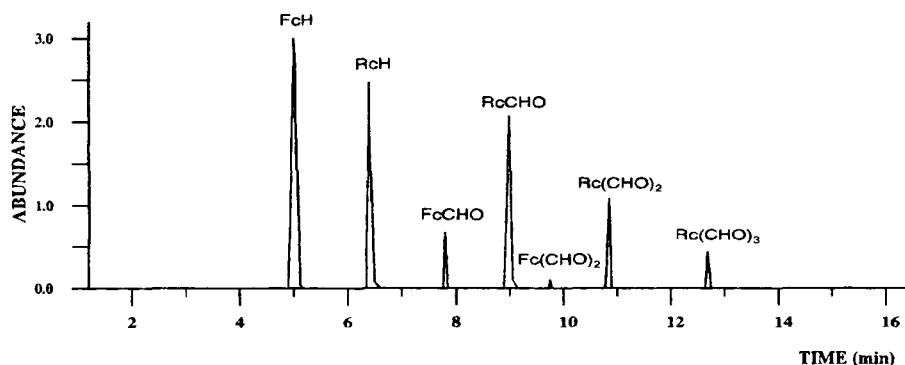


Fig. 1. The GC spectrum of products of a competitive lithiation reaction containing equimolar amounts of ferrocene and ruthenocene.

Table 2
Some lithiations of ruthenocene under varying conditions

RLi (type)	RcH/RLi (ratio)	KOt-Bu (vs. RcH)	Temp. (°C)	Time (min)	RcH/Rc(CHO)/Rc(CHO) ₂ (percentage of original RcH)	Comments
<i>t</i> -BuLi	1:1.5	0	0	20	4.0:90.5:3.0	Ref. [1]
<i>t</i> -BuLi	1:1.5	0	0	20	39.0:48.0:13.0	
<i>t</i> -BuLi	1:1.5	0	−20	170	54.0:31.0:— ^a	
<i>t</i> -BuLi	1:4.0	0	−50	240	82.0:13.0:— ^a	
<i>t</i> -BuLi	1:1.5	0.125	−74	60	22.7:70.9:0.9	
<i>t</i> -BuLi	1:2.0	0.125	−74	60	23.3:69.0:0.5	
<i>t</i> -BuLi	1:2.0	0.125	−74	15	24.0:72.0:3.8	
<i>t</i> -BuLi	1:2.0	0.125	−74	30	13.3:80.9:4.3	

^a Yields of more highly substituted aldehydes were not determined.

vealingly disappointing; the product distribution was 39% RcH, 48% ruthenocene carboxaldehyde, 13% ruthenocene dialdehyde, and a minor amount of ruthenocene trialdehyde. A repeat of this reaction produced rather similar product distribution. It thus seems impossible to accept that even the most skilled and fortunate chemist could have achieved the published 91.5% yield of the monoaldehyde.

Lithiation of ruthenocene with a stoichiometric *t*-BuLi/KOt-Bu mixture also met with failure: all *t*-BuLi had been consumed, ruthenocene was recovered in 20% yield, and all three ruthenocene carboxaldehydes were formed, with the mono- and dialdehydes being produced in nearly equal proportions of 30 and 34% respectively.

Again, the use of substoichiometric amounts of KOt-Bu led to better success. In a first attempt using molar ratios of ruthenocene/*t*-BuLi/KOt-Bu of 1:1.5:0.125, the monoaldehyde was obtained in 71% yield and only 1% of the dialdehyde was formed, but the product mixture contained 23% of ruthenocene. A reaction with 2 equiv. *t*-BuLi under otherwise equivalent conditions produced a similar result: 23% unreacted ruthenocene, 70.5% monoaldehyde, 0.5% dialdehyde, and a trace of trialdehyde. The presence of ruthenocene in spite of its high reactivity led us to consider the possibility that lithioruthenocenes, especially in the presence of KOt-Bu, were reacting with THF faster than lithioferrocenes, and that therefore the reaction time had to be shortened. Cutting the reaction time in half (to 30 min) reduced the amount of recovered ruthenocene to 13%, gave an 81% yield of the monoaldehyde and only 4% of the dialdehyde; only a trace amount of trialdehyde was observed. However, cutting the reaction time to 15 min led to incomplete lithiation and 24% of unreacted ruthenocene. The results of these experiments are summarized in Table 2.

3. Summary

It is unfortunately rather evident that the monolithiation procedures we published in 1993 for ferrocene and

ruthenocene are far from the now firmly established reality that under the given conditions a much more complicated reaction occurs, which leads to a product mixture rather than to 90 + % yields of a single product. With the knowledge that these lithiation reactions depend on a set of hard-to-analyze variables, there remains a distant possibility that an unusual coincidence of circumstances may have led to exceptionally high yields of products derived from specific monolithiation for the case of ferrocene, but the evidence presented here makes this highly unlikely, even more so for the ruthenocene case.

We were able to define a set of reaction conditions, employing a *t*-BuLi/KOt-Bu “super base” pair at low temperature, which allows the monolithiation of ferrocene in greater than 90% yield. This set of conditions can also be transferred to the more reactive ruthenocene, and the monoaldehyde can be obtained in better than 80% yield.

4. Experimental

4.1. General

All reactions involving air- or moisture-sensitive reagents were carried out under a positive pressure of nitrogen. Reagents and solvents were used as-received from commercial sources, except for the following: THF was distilled from potassium/benzophenone; hexane was distilled from potassium. Melting points were recorded on a hot stage apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AC 270 Spectrometer in CDCl₃ with 1% TMS as an internal standard. GC-MS spectra were obtained on a Hewlett-Packard 5970B GC/MS instrument. Analytical TLC was carried out with Baker-flex Silica Gel IB-2 plates. Flash column chromatography was performed with silica gel (60–200 mesh) manufactured by J.T. Baker Chemical Co. The commercially available lithium compounds *n*-butyllithium, *s*-butyllithium, and *t*-butyllithium were calibrated according to the literature method prior to use.

4.2. Preparation of monolithio ferrocene and ferrocene carboxaldehyde using *t*-BuLi and *t*-BuOK

In a nitrogen-flushed three-necked flask with addition funnel, stirrer, and reflux condenser, ferrocene (8.0 g, 43.0 mmol) and potassium *t*-butoxide (0.60 g, 5.34 mmol) were dissolved in 400 ml of dry THF and the solution was cooled to -74°C in a dry ice/acetone bath. Over a period of 15 min, 50.6 ml (86.02 mmol) of 1.7 M *t*-BuLi were added, while ensuring the temperature remained below -70°C . The mixture was stirred at this temperature for 1 h. DMF (8.0 ml, 100.8 mmol) was added while keeping the solution at -74°C . The cooling bath was removed and the solution allowed to warm to -40°C over a period of approximately 20 min. At this point the solution was hydrolyzed with demineralized water, which turned the reaction mixture deep red. THF and *t*-butanol were removed under reduced pressure, then the aldehyde was extracted with several portions of CH_2Cl_2 . The extracts were combined, washed with water, and dried over MgSO_4 . Products were separated by flash chromatography. Silica gel, (deactivated by addition of 4% w/w water) was used as the stationary phase. The following series of solvents was employed: (1) hexane to remove ferrocene; (2) CH_2Cl_2 to remove ferrocene monoaldehyde; (3) CH_2Cl_2 /diethyl ether 1:1 to remove ferrocene dialdehyde. Yields, based on ferrocene: ferrocene carboxaldehyde, 8.35 g (90.7%); ferrocene-1,1'-dialdehyde, 510 mg (4.9%), ferrocene, 320 mg (4.0%). Characterization: m.p. 121°C . [Ref. [7] 123.5°C]; ^1H NMR (CDCl_3): δ 4.81 (2 H, t, Cp), 4.6 (2 H, t, Cp), 4.29 (5 H, Cp). 9.95 (1 H, s, CHO); MS: M/e 214 (M^+), 186 ($\text{M}-\text{CO}^+$), 121 (CpFe^+), 56 (Fe^+).

4.3. Examination of possible lithium exchange reaction between ferrocene, monolithioferrocene, and dilithioferrocene

In a nitrogen-flushed three-necked flask with addition funnel, stirrer, and reflux condenser, ferrocene (8.00 g, 43.0 mmol) and potassium *t*-butoxide (4.80 g, 42.7 mmol) were dissolved in 350 ml of dry THF. This solution was cooled to -74°C in a dry ice/2-propanol bath. Over a period of 15 min, 37.8 ml (42.9 mmol) of 1.135 M *t*-BuLi were added, while ensuring the flask temperature remained below -70°C . The reaction mixture was stirred at this temperature for 2 h. At this point approximately 50% of the reaction mixture was transferred via cannula to a nitrogen-flushed flask containing 1.25 ml (16.1 mmol) DMF in 50 ml THF at -74°C . This portion was permitted to warm slowly to -10°C and then hydrolyzed with demineralized water. To the remaining portion, an additional 4.00 g (21.5 mmol) ferrocene was added and allowed to react for one additional hour. DMF (2.0 ml, 25.1 mmol) was then

added, while keeping the solution at -74°C . The cooling bath was removed and the solution allowed to warm to -40°C over a period of approximately 20 min. This reaction mixture was then hydrolyzed with demineralized water. For each fraction, THF and *t*-butanol were removed under reduced pressure, then the aldehydes were extracted with several portions of CH_2Cl_2 . Each mixture was washed with water, and dried over MgSO_4 . Components of each fraction were separated over a short silica gel column in the same manner as in the monoaldehyde synthesis above. The product distribution in the first portion was 2.7 mmol ferrocene, 6.0 mmol monoaldehyde, 1.9 mmol dialdehyde; in the second portion the distribution was 33.5 mmol, 15.9 mmol, 4.6 mmol.

4.4. Competitive lithiation reaction of ferrocene and ruthenocene

In a nitrogen-flushed three-necked flask, with stirrer and reflux condenser, ferrocene (0.40 g, 2.16 mmol) and ruthenocene (0.50 g, 2.16 mmol) were dissolved in 100 ml of dry THF. This solution was cooled to -74°C in a dry ice/1-propanol bath. Over a period of 5 min, 7.6 ml (12.9 mmol) of 1.7 M *t*-BuLi were added, ensuring the flask temperature remained below -70°C . The solution was allowed to warm to -30°C and then stirred at this temperature for 3 h. DMF (1.5 ml, 19.0 mmol) was then added, the cooling bath removed, and the solution allowed to warm to -10°C . Next, the reaction mixture was hydrolyzed with demineralized water. THF was removed under reduced pressure, and the product mixture was extracted with several portions of CH_2Cl_2 . The extracts were combined, washed with water, and dried over MgSO_4 . The ferrocene/ruthenocene fractions were separated through flash chromatography. Silica gel (deactivated with 4% w/w water) was used with hexane as eluent. The quantity of recovered metallocenes was determined through the total mass of the combined compounds (0.24 g (60%) ferrocene, 0.13 g (26%) ruthenocene), and gas-chromatography peak integration. To avoid errors due to integration differences, the peak area integration of a sample of the ferrocene/ruthenocene mixture was compared with a 1:1 standard, run immediately beforehand. The relative molar concentration was then determined, converted to a gram ratio, and scaled to the total mass of the product mixture. A second, independently prepared standard yielded a correction factor within 1% of the first.

4.5. Preparation of monolithio ruthenocene and ruthenocene carboxaldehyde using *t*-BuLi and *t*-BuOK

In a nitrogen-flushed three-necked flask with addition funnel, stirrer, and reflux condenser, ruthenocene (1.50 g, 6.49 mmol) and potassium *t*-butoxide (0.09 g,

0.80 mmol) were dissolved in 200 ml of dry THF and the solution was cooled to -74°C in a dry ice/acetone bath. Over a period of 10 min, 7.6 ml (12.92 mmol) of 1.7 M *t*-BuLi were added, while ensuring the flask temperature remained below -70°C . The solution turned pale-yellow following addition. The mixture was then stirred at -74°C for 26 min. DMF (1.3 ml, 16.4 mmol) was added while keeping the solution at -74°C . The cooling bath was removed and the solution allowed to warm to -40°C over a period of approximately 10 min. At this point, the solution was hydrolyzed with demineralized water. THF and *t*-butanol were removed under reduced pressure, then the aldehyde was extracted with several portions of CH_2Cl_2 . The extracts were combined, washed with water, and dried over MgSO_4 . Products were separated by chromatography using the same solvent series as in the ferrocene carboxaldehyde synthesis. Yields, based on ruthenocene: ruthenocene carboxaldehyde, 1.36 g (80.9%); ruthenocene-1,1'-dialdehyde, 80 mg (4.3%), ruthenocene, 200 mg (13.3%). Characterization: m.p. 100°C . [Ref. [8] $100.2\text{--}100.8^{\circ}\text{C}$]; ^1H NMR (CDCl_3): δ 4.58 (5 H, s, Cp), 4.79 (2 H, t, Cp), 5.02 (2 H, t, Cp), 9.66 (1 H, s, CHO) ppm; MS: M/e 260 (M^+), 232 ($\text{M}-\text{CO}^+$), 167 (CpRu^+).

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