Coordination chemistry of perhalogenated cyclopentadienes and alkynes

XVIII. * Mechanistic studies on the metal–halogen exchange reaction of ring-halogenated metallocenes: the influence of stoichiometry, temperature, solvent and reaction time

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Abstract

When $[C_5Br_5]Mn(CO)_3$ (1) is treated with butyllithium and hydrolyzed after some time, one can always obtain more than one product, independent of stoichiometry, solvent, temperature and lithiation time. However, the distribution of products strongly depends on the reaction conditions. For example, in THF, with a tenfold excess of butyllithium at $-78°C$, a conversion of more than 80% into $[C_5H_5]Mn(CO)_3$ can be achieved. In $[C_5Cl_4Br]Mn(CO)_3$ (2) only a maximum of two halogens can be substituted by hydrogen. These results can be explained in terms of the competition between butyl lithium and the lithiated species $[C_5X_4Li]Mn(CO)_3$ in the halogen–metal exchange reaction.

Key words: Manganese; Lithium; Cyclopentadienyl; Carbonyl; Metal–halogen exchange

1. Introduction

The halogen–metal exchange reaction is a very valuable tool for the synthesis of functionalized aromatics, since it can be performed under very mild conditions [2] (eqn. (1)):

$$Ar–X + Li–R \rightleftharpoons Ar–Li + R–X \qquad (1)$$
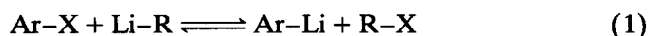
In the chemistry of ferrocene, the exchange reaction of bromoferrocene with butyllithium is still the best method for obtaining pure monolithiated ferrocene [3]. However, whereas monochlorferrocene is deprotonated exclusively by butyl lithium instead of undergoing halogen–metal interchange, the higher chlorinated ferrocenes undergo both reactions simultaneously, thus leading to complex product mixtures [4]. This observation shows two difficulties that are involved in the halogen–metal exchange reaction, namely the low re-activity of chlorine substituents, and the complications with polyhalogenated systems. In the latter LiX-elimination can sometimes lead to an aryne intermediate [5], but also to complicated transhalogenations, frequently referred to as "halogen-dance reactions" [6]. Quite surprising is the formation of $[C_6Li_6]$ from C_6Cl_6, which has been reported recently [7].

As we were already using the halogen-metal exchange reaction as a synthetic tool for the synthesis of polyfunctionalized metallocenes [8], we became interested in the mechanism of these reactions as well as in exploiting the synthetic potential of them. Here we report some mechanistic studies on the reaction of pentahalocymantrenes with butyl lithium.

2. Results

A few years ago, we started to make use of the halogen–metal exchange reaction for the synthesis of functionalized cymantrenes by treating $[C_5Cl_4Br]Mn(CO)_3$ (2) with butyl lithium and an appropriate electrophile.

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* For Part XVII see ref. [1].
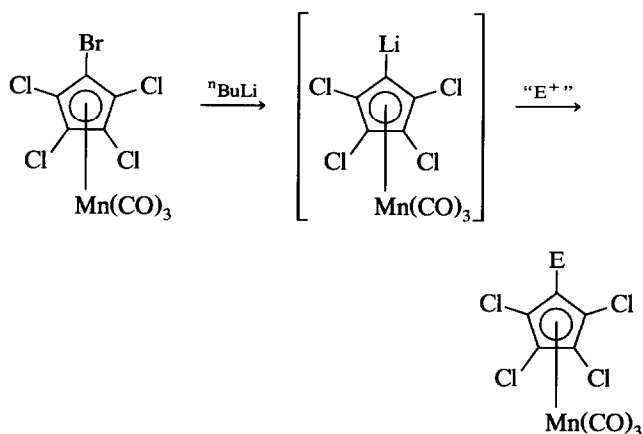
Isolated yields over 80% could be obtained, with an average yield of about 70% [8a,b]. We found that the remaining chlorine substituents only reluctantly underwent further metal–halogen exchange, and thus polyfunctionalized derivatives could only be obtained when the "first" electrophile contained a sulfur, selenium or phosphorous function [8c–f]. We therefore switched to using [C5Br5]Mn(CO)3 (1), and with this a stepwise synthesis of polysilylated cymantrenes could be achieved, with the aid of the halogen–metal exchange, with isolated yields of 80–90% for each step [8h,i,k].

Although we were quite satisfied with the resulting yields, we wondered what had happened to the rest of the starting materials. Thus, we had a closer look at the ¹H-NMR spectra of the raw reaction products (of which the solvent had been evaporated off and the residue extracted by the NMR solvent). As expected, there were one or two minor peaks (of 5–10% intensity) close to the main peaks of the desired compounds, indicating that there had been more than one product formed in most of the reactions reported previously by

TABLE 1. Hydrolysis products of 1 + x BuLi in Et_2O, 5 min at −78°C

Compd.	x							
	0.8	1	2	3	7	10	20	30
3	91	78	23	8	5	0	0	0
4a	6	15	73	52	32	21	3	4
4b	3	7	0	0	7	0	0	0
5a	0	0	4	31	37	32	16	22
5b	0	0	0	6	0	9	0	0
6	0	0	0	3	19	32	22	9
7	0	0	0	0	0	6	59	65

us. Therefore, it seemed necessary to find out how the reaction conditions influenced yields and reactivities. We decided to start with elimination of steric effects first and to examine only the smallest electrophile, the proton. As a proton source we used water and methanol. Soon it became clear that below −50°C H_2O became only an unreactive solid and did not protonate our lithiation mixtures. As we were primarily interested in the lithiation step, a fast reaction with the electrophile at low temperatures was required, and therefore the use of MeOH was preferred. We then started our experiments with the perbrominated complex 1.

The reaction parameters we chose to study were *stoichiometry*, *solvent*, *temperature* and *reaction time*. The variation in stoichiometry 1:BuLi varied from 1:0.8 to 1:20, the solvents were n-hexane, Et_2O and THF, the temperatures were −78°C and −50°C, and lithiation times were 5 min and 60 min, but not all combinations were verified. All reactions were run under the same conditions (see *Experimental section*). The composition of the products was determined by
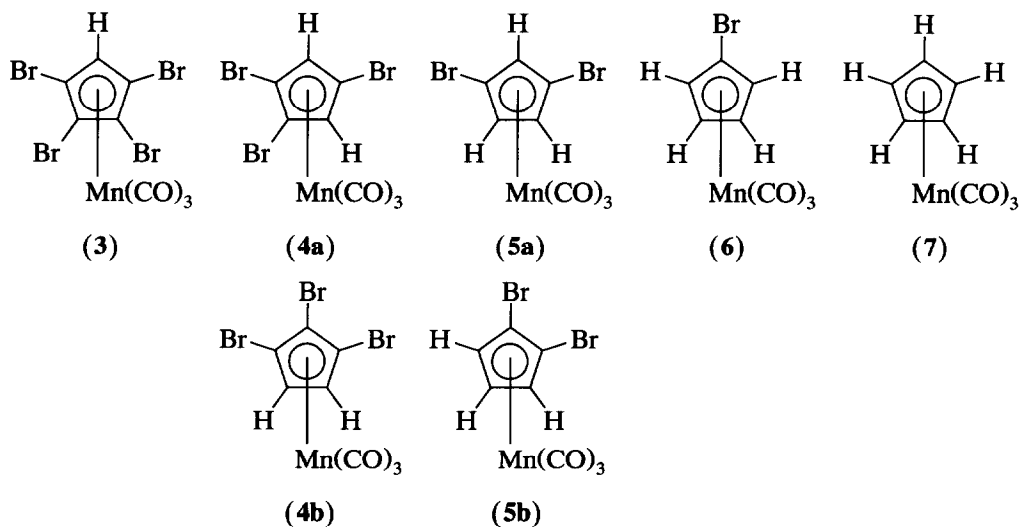

Scheme 1.

TABLE 2. Hydrolysis products of $1+x$ BuLi in Et_2O, 60 min at $-78°C$

Compd.	x		
	3	7	10
3	14	4	0
4a	39	27	10
4b	0	0	0
5a	40	44	27
5b	10	10	0
6	0	16	42
7	0	0	21

TABLE 4. Hydrolysis products $1+x$ BuLi in hexane, 5 min at $-78°C$

Compd.	x			
	1	3	7	10
3	86	49	41	28
4a	11	29	31	23
4b	3	13	10	10
5a	0	5	10	17
5b	0	4	5	9
6	0	1	3	9
7	0	1	1	4

^1H-NMR spectroscopy. For the purpose of identification, the known [9] complexes $[C_5Br_{5-n}H_n]Mn(CO)_3$ ($n = 1-5$), 3, 4a, 5a, 6 and 7, were prepared independently and characterized by ^1H NMR and ^{13}C NMR spectroscopy (Scheme 1). The results of these experiments are summarized in Tables 1–5.

2.1. Influence of stoichiometry

Even with careful weighing, addition of one equivalent of ^nBuLi in Et_2O or hexane led to three products: 3, 4a and a third compound that was not among the five bromocymantrenes that had been prepared in a directed synthesis. Since there are two more isomeric bromocymantrenes possible, i.e. 1,2,3-tribromocymantrene (4b) and 1,2-dibromocymantrene (5b), it seemed plausible, also in accordance with the ^1H-NMR chemical shifts, that the third product was the isomeric disubstituted product 4b. The amount of dilithiation and the regioselectivity for 4a/b strongly depended on the solvent (see below). When three equivalents of BuLi were used, a mixture of all bromocymantrenes, except 7 was obtained in all solvents at $-78°C$, with the relative amounts highly dependent on the solvent. With 10 or more equivalents of BuLi 7 could also be detected in all solvents, again with a large influence of the solvent on the relative amount. However, even when only 0.8 equivalents of BuLi were used in Et_2O at $-78°C$, there was still 9% formation of the disubsti-

tuted products 4a and 4b, with a site selectivity of approximately 2:1. With regard to the general regioselectivity of 4a/b and 5a/b, there seemed to be an increase with increasing number of equivalents of BuLi.

2.2. Influence of solvent

With the exception of 1:1 stoichiometry, the amount of products derived from higher lithiated species always increased on going from hexane to Et_2O and THF. This is particularly obvious in the case of 7:1 stoichiometry, where the amount of products 6 and 7 makes up for only 5% in hexane, for 18% in Et_2O, but for 55% in THF. Furthermore, there seems to be an increase in regioselectivity with regard to the pairs 4a/b and 5a/b on going from hexane to Et_2O and THF. When equivalent amounts of 1 and BuLi were reacted at $-78°C$, the amount of disubstituted products became much higher in hexane than in Et_2O.

2.3. Influence of reaction time and temperature

This was only tested in Et_2O. Increasing the time of lithiation from 5 min to 60 min at $-78°C$ led to a higher degree of lithiation, particularly when a larger excess of BuLi was used, although the regioselectivity was not effected. Performing the lithiation step at $-50°C$ had an even more drastic effect. For example, for 7:1 stoichiometry the amount of tetra- and penta-substituted products 6 and 7 increased from 18% to

TABLE 3. Hydrolysis products of $1+x$ BuLi in Et_2O, 5 min at $-50°C$

Compd.	x		
	3	7	10
3	0	0	0
4a	25	14	16
4b	0	0	0
5a	61	34	54
5b	4	5	4
6	11	33	25
7	0	14	1

TABLE 5. Hydrolysis products of $1+x$ BuLi in THF, 5 min at $-78°C$

Compd.	x			
	3	7	10	20
3	8	0	0	0
4a	66	17	3	5
4b	3	0	0	0
5a	17	24	17	7
5b	3	4	0	0
6	3	20	9	4
7	0	35	71	84

TABLE 6. Hydrolysis products of 2 + x BuLi, 5 min at −78°C

solvent	Compd.	x		
		2	3	10
Et$_2$O	8	93	93	80
	9a	6	6	14
	9b	1	1	6
THF	8		84	2
	9a		11	98
	9b		5	0

47%. However, when a larger excess of BuLi was used, the situation changed again, since mainly decomposition reactions took place and the absolute yields decreased markedly. Similar results were obtained when water was used as a proton source.

To get further insight in the mechanism of the reaction operating here, we also examined the reactivity of [C$_5$Cl$_4$Br]Mn(CO)$_3$ (2) (see Table 6). In hexane a white precipitate formed with BuLi, presumably "[C$_5$Cl$_4$Li]Mn(CO)$_3$" (2a), which dissolved upon addition of MeOH and only gave [C$_5$Cl$_4$H]Mn(CO)$_3$ (8) after workup. In Et$_2$O, even with a large excess of BuLi, monosubstitution remained the main reaction, but two by-products could be detected. By comparison with 1, we assumed that these compounds were the two isomeric trichlorocymantrenes [C$_5$Cl$_3$H$_2$]Mn(CO)$_3$ (9a, 9b). The maximum yield of these disubstitution products is 20%, with a loss of regioselectivity of 9a/b when the excess of BuLi is increased. In THF, the increase of the amount of BuLi up to stoichiometric ratio of

10 : 1 leads to > 98% conversion to the disubstitution product 9a, with no other products (besides ca. 2% 8).
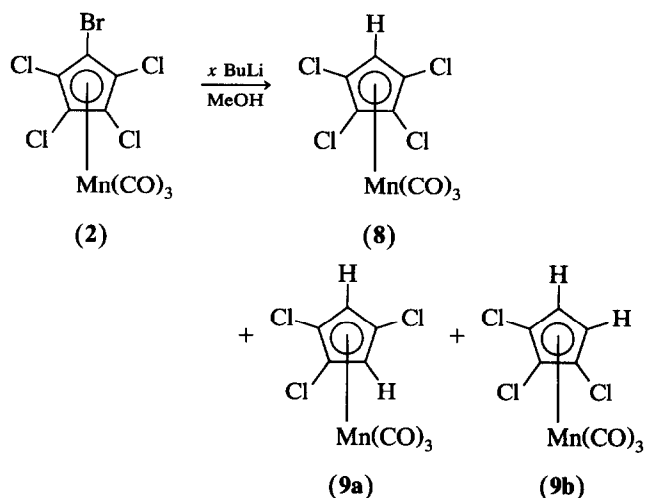
3. Discussion

As could be expected from our earlier preparative studies (and also from related studies of "purely organic" compounds [10]), the tetrachlorocymantrene 2 is much less reactive than the perbrominated analogue 1. However, it is very surprising that no more than two halogen substituents can be replaced, no matter what the stoichiometry or the solvent is. The nature of the intermediate lithiated species could possibly provide an explanation for this behaviour. There are basically three mechanisms that have been discussed for the metal–halogen exchange reaction [2]:
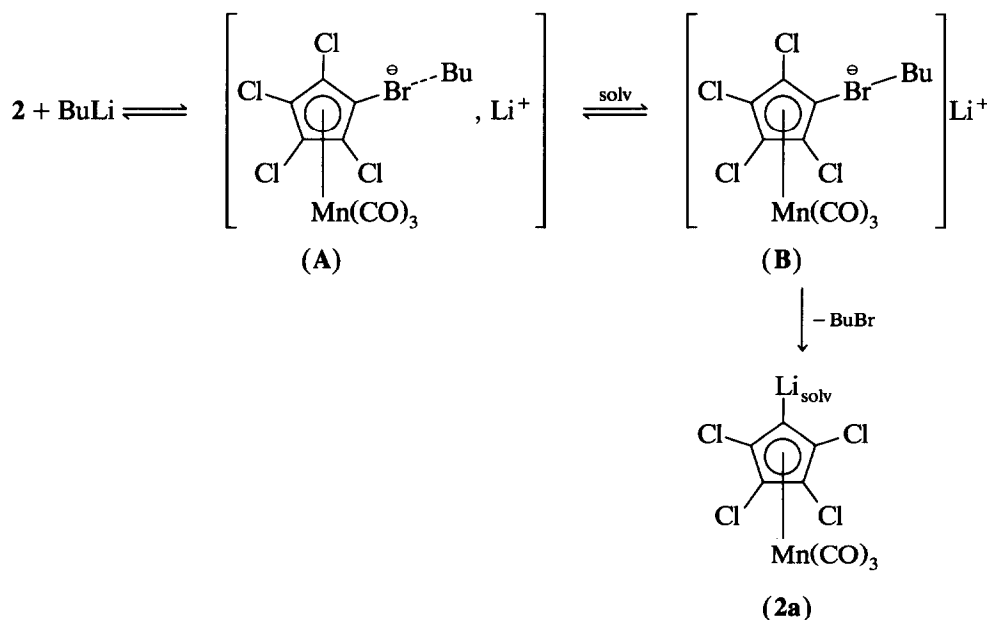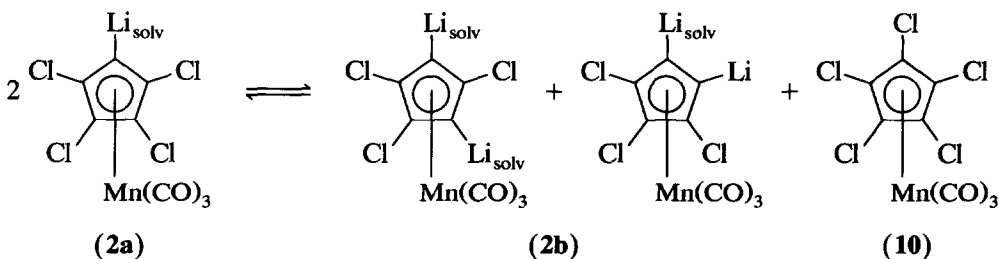

Scheme 2.

(a) A four-centre transition state, with lithium and halogen bonded to both carbanionic centres.

(b) A SET mechanism, which had been discussed and discarded for the reaction of chloroferrocene with butyl lithium [11].

(c) The third, and nowadays most favoured one, is a nucleophilic "ate"-mechanism, in which the halogen is bonded to both carbanionic residues, with the lithium attached either in a close contact or a solvent separated ion pair. The latter mechanism would lead to transition states or intermediates like (A) or (B) in Scheme 2.
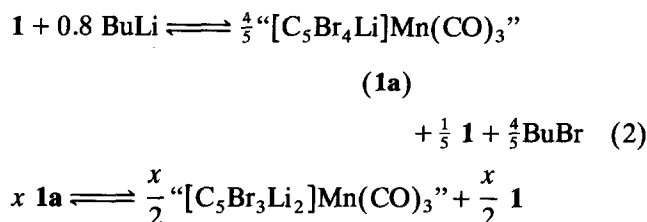
The effect of different solvents must be seen in the light of the following two aspects. First, butyl lithium is not a monomer, but an aggregate in solution, e.g. a hexamer in hexane [12]. Going to more polar solvents breaks these aggregates down, and enhances the reactivity of the butyl carbanion. Second, the stability of the ion pairs (A) and (B) is affected by the solvent system used. While (A) might be precipitated by the solvent hexane and thereby be protected from further attack by BuLi, ethereal solvents most likely transform it into the separated species (B). In hexane, formation of (B) is unlikely; still, (A) might gradually lose BuBr leaving a very reactive unsolvated species 2a. In ether solvents, the separated anionic "ate" moiety (B) might either be stable or generate a solvated species $[C_5Cl_4Li^*$ $(OR_2)_n]Mn(CO)_3$ (2a), which could subsequently be attacked by BuLi to give a new "ate" complex. Alternatively, two molecules of 2a could react with one another, leading to a mixture of a dilithiated species $[C_5Cl_3Li^*_2(OR_2)_m]Mn(CO)_3$ (2b) and $[C_5Cl_5]Mn(CO)_3$ (10) (Scheme 3).

To test the latter possibility, the reaction product of 2 with ^nBuLi in hexane, either 2a or the "ate" complex (A), was isolated, redissolved in THF and hydrolyzed. It showed that the product mixture contained 8, 9a, 9b and 10, exactly as predicted by the mechanism depicted in Scheme 3. Compound 10 was identified by ^{13}C NMR spectroscopy (and was not present in the starting material, 2!). It should also be noted here that both isomers 9a + b are formed, while (see Table 6) a large excess of ^nBuLi and 2 in THF yields only 9a.

Also the result of the reaction of perbromocymantrene 1 with 0.8 equivalents ^nBuLi can be easily understood in terms of an intermolecular lithium–bromine exchange between two lithiated species (eqn. (2)):

$$1 + 0.8\ BuLi \rightleftharpoons \tfrac{4}{5}"[C_5Br_4Li]Mn(CO)_3"$$

$$(1a)$$

$$+ \tfrac{1}{5}\,1 + \tfrac{4}{5}BuBr \quad (2)$$

$$x\ 1a \rightleftharpoons \frac{x}{2}"[C_5Br_3Li_2]Mn(CO)_3" + \frac{x}{2}\,1$$

After hydrolysis, the reaction mixture should contain (0.8 − X) mol 3, (0.2 + 0.5 X) mol 1 and 0.5 X mol of 4a + b per mol of 1 used in the reaction. From the integration of the ^1H-NMR signals for 3, 4a and 4b X can be estimated to be 0.13. (Although integration of ^{13}C NMR signals is not a reliable method owing to different relaxation times, a rough estimate can be made by comparison of the intensity of the one C–Br signal for 1 and the two C–Br signals for 3. This leads to a value of 0.11 for X, which agrees well with the result obtained above.)

The next question arising is how the higher substitution products are formed in the perbromocymantrene system. One possibility is that butyl lithium undergoes multiple lithium–bromine exchange with 1 under formation of polylithiated complexes $[C_5Br_{5-n}Li_n]Mn$ $(CO)_3$ (n = 1–5) or the corresponding "ate" complexes. Alternatively, a sequence of intermolecular Li/Br transfers as shown in Scheme 3, but starting from a monolithiated cymantrene, leads to a build-up of these polylithiated species.

To test these possibilities, two control experiments were performed (entries 1 and 2 in Table 7).

First, the lithiated chlorocymantrene 2a (or (A)) was isolated, mixed with 25 mol% 1, dissolved in THF at −78°C and hydrolyzed after 10 min. The ^1H NMR spectroscopic examination of the product mixture showed that all bromocymantrenes 3–7 had formed (entry 1). No derivative with H and Cl on the same ring could be detected. The regioselectivity for the pairs

(2a)   (2b)   (10)

Scheme 3.

TABLE 7. Control experiments

Compd.	Entry			
	1	2	3	4
3	26	4	29	75
4a	31	43	9	18
4b	7	0	12	5
5a	16	35	12	3
5b	7	4	6	0
6	9	13	11	0
7	4	1	21	0

4a/b and **5a/b** was much lower (roughly 4 : 1 and 2 : 1) in comparison with the result of the ^{n}BuLi reaction with 3 : 1 stoichiometry (Table 5). In another experiment, **1** was treated with 20 equivalents ^{n}BuLi in Et$_2$O at −78°C and after 5 min with methylcyclohexane. After the ether was evaporated *in vacuo*, the lithiated species soon precipitated and were isolated. After washing with pentane, they were suspended in pentane and hydrolyzed with MeOH. This procedure normally "preserves" the lithiated species in the THF solution, owing to their expected low solubility in an alkane solvent. The ^{1}H NMR spectroscopic examination showed (entry 2) that only a small amount of the tetra- and pentasubstitution products **6** and **7** had formed (14% compared to 38% without precipitation of the lithiated species, Table 1), the main constituents being di- and trisubstituted species (82%).

Obviously, primarily only bis- and tris-lithiated species are formed, both directly with ^{n}BuLi and from Li–Br exchange between two lithiated cymantrenes. In a coordinating solvent, especially when longer reaction times and/or higher temperatures are possible, these might then react further with each other, yielding the higher substituted products. However, the gradual build-up of negative charge should prevent further nucleophilic attacks by carbanionic species, especially in a non-coordinating solvent like hexane, so the formation of a pentalithiated species does not seem very likely. But there is an alternative pathway that could explain the pentasubstituted product. It is known that lithium-halide-exchange is a very fast reaction, sometimes faster than hydrolysis reactions [13]. If we assume
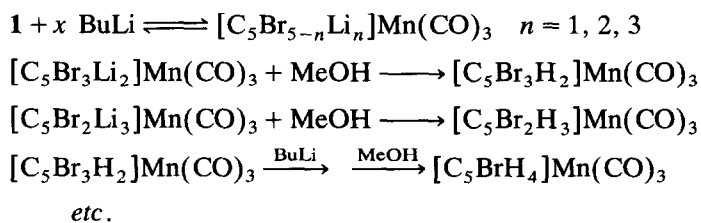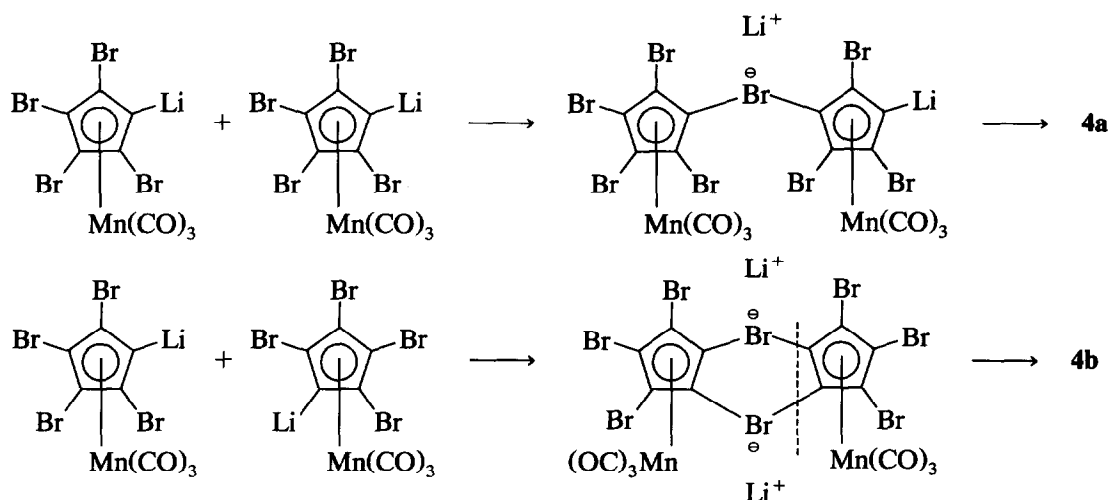
further that the basicity of the lithiated cymantrenes is much higher than the basicity of ^{n}BuLi, it seems possible that the lithiated cymantrenes are protonated by MeOH while the BuLi remains unaffected. These hydrolyzed species might then undergo further bromine–lithium exchange, become hydrolyzed, *etc.* (Scheme 4)

To test for this possibility another control experiment was performed (entry 3 in Table 7). Methanol was added to a solution of **1** in THF at −78°C, followed by addition of 10 equivalents of ^{n}BuLi. After work-up the ^{1}H NMR spectroscopic examination of the reaction mixture revealed that still 21% of the penta-substitution product **7** had formed, which is of course less than in the experiment with MeOH added *after* BuLi (71%, Table 5). When MeOH is present in the early stages of the lithiation step, formation of species with two or three Li substituents might be slowed down owing to hydrolysis of the monolithiated species. Thus, more steps become necessary to yield the fully hydrolyzed species.

Two more aspects of these experiments should be discussed shortly. *What is the nature of the lithiated species?* The final proof might come from a crystal structure-determination of the precipitate formed from **2** and BuLi in hexane, but so far any crystallization attempts lead only to isolation of its hydrolysis product **3**. A combined ^{7}Li–^{13}C–^{1}H NMR study of the reaction mixtures might give insight in the species present into solution, but so far we were not able to obtain such spectra. At least one hint comes from another control experiment (entry 4 in Table 7). When the reaction of **1** with one equivalent of ^{n}BuLi in Et$_2$O is performed in a highly diluted solution, a slight increase in the amount of higher substitution products can be observed, particularly 3% formation of a trisubstitution product, which could not be detected in the more concentrated solution. Working in a more dilute solution should favour the formation of solvent-separated ion pairs like (**B**) in Scheme 2. If this leads to higher substitution products, the active species for carrying on the substitution process must be something like (**B**) or the covalent **2a** derived from it.

The other aspect concerns the *regioselectivity* in the di-and trisubstitution process. For large excesses of

$$1 + x \; \text{BuLi} \; \rightleftharpoons \; [C_5Br_{5-n}Li_n]Mn(CO)_3 \quad n = 1, 2, 3$$

$$[C_5Br_3Li_2]Mn(CO)_3 + \text{MeOH} \longrightarrow [C_5Br_3H_2]Mn(CO)_3$$

$$[C_5Br_2Li_3]Mn(CO)_3 + \text{MeOH} \longrightarrow [C_5Br_2H_3]Mn(CO)_3$$

$$[C_5Br_3H_2]Mn(CO)_3 \xrightarrow{\text{BuLi}} \xrightarrow{\text{MeOH}} [C_5BrH_4]Mn(CO)_3$$

etc.

Scheme 4.

Scheme 5.

BuLi, the formation of the 1,3- and 1,2,4-substituted products seems clearly to be favoured, the other isomers sometimes being below the detection limit of the spectra. To an even higher extent this seems to be true for the reactions run at higher temperatures or with longer lithiation times.

Obviously, the isomers 4a and 5a are formed preferably when the system has the chance to equilibrate, which means that they must be thermodynamically more stable. Since the metal–halogen exchange reaction is reversible in principle, the excess of BuLi might also induce the transformations 4b → 4a and 5b → 5a. With butyl lithium these isomers are also formed under kinetic control, while the lithiated cymantrenes – which are most likely to be the predominant species with the lower stoichiometric ratios, in the solvent hexane and, of course, when they are isolated and used as such – also seem to yield appreciable amounts of the isomers 4b and 5b. This might be explained in terms of the formation of a cyclic double "ate" transition state or intermediate as shown in Scheme 5.

Although there is no precedent for such a compound, its formation seems geometrically possible, and the stability of "ate" complexes of perhalogenated aromatics is well documented [14]. However, for the moment the only "proof" of its existence is the fact that it can readily explain the selectivity observed.

4. Conclusion

When the pentahalocymantrenes $[C_5X_4Br]Mn(CO)_3$ are treated with an excess of butyl lithium and the reaction mixture then hydrolyzed, the product distribu-

tion will be mainly influenced by three different processes:

(1) Single or multiple lithium–halogen exchange with BuLi leading either to covalent lithiocymantrenes $[C_5X_{5-n}Li_n]Mn(CO)_3$ or "ate" complexes, which might be transformed to the former ones by action of coordinating solvents. A lithiation degree $n > 3$ seems unlikely.

(2) Intermolecular lithium–halogen exchange between two lithiated cymantrenes with a different regioselectivity from the BuLi-induced process, which can gradually build up highly lithiated species as in (1).

(3) Hydrolysis of the intermediate lithiated species before the maximum degree of lithiation is reached, but also before the BuLi is hydrolyzed. The bromocymantrenes $[C_5H_{5-n}Br_n]Mn(CO)_3$ formed in this way can undergo further Li–Br exchange with BuLi and/or lithiated cymantrenes, until finally all bromine substituents have been replaced by hydrogen.

For the synthetic applications of the studies presented here (of course, there are simpler ways of producing cymantrene 7!) the right balance between these three processes (or a process related to (3) for other electrophiles) seems crucial. The maximum amount of Li substituents that can be introduced by processes (1) or (2) may be an upper limit for the degree of substitution by this method. After the electrophile has substituted the lithium, attack of BuLi might occur at the new substituent instead of at the halogen, or steric hindrance in the newly generated "ate" complexes might prevent further substitutions.

Studies on the influence of the electrophile and of the type of halometallocene used are currently in progress and will be published soon.

5. Experimental details

The reactions were performed in standard Schlenk tube techniques under dry nitrogen, using freshly distilled solvents (from $LiAlH_4$, under N_2). The starting materials 1 and 2 were prepared according to literature [15]. A 1.6 M solution of ^nBuLi in hexane (Aldrich) was used in all experiments. The ^1H-NMR and ^{13}C-NMR spectra were measured in C_6D_6, using a *Jeol GSX-270* spectrometer, operating at 270 MHz (^1H) and 67.9 MHz (^{13}C); chemical shifts (δ) are referred to the solvent signals (7.150 ppm for ^1H and 128.0 ppm for ^{13}C).

5.1. Tricarbonyl(tetrabromocyclopentadienyl)manganese (3)

A solution of 0.500 g of 2 (0.84 mmol) in 10 ml of Et_2O is treated at $-78°C$ with 0.52 ml of a BuLi solution (0.84 mmol). After 30 min *ca.* 0.2 ml H_2O is added and the solution warmed to room temperature within 15 min. The solvent is then evaporated *in vacuo* and the residue treated with hexane and Na_2SO_4. The suspension is filtered through silicagel, the eluate concentrated to about 5 ml and then cooled ($-20°C$) to give a yellow microcrystalline powder. ^1H NMR: 3.98 ppm. ^{13}C NMR: 221.8 (MnCO), 88.2, 85.2, 81.5 (C_5) ppm.

5.2. Tricarbonyl(1,2,4-tribromocyclopentadienyl)manganese (4a)

1.000 g of 1 (1.68 mmol), dissolved in 10 ml of Et_2O, are first treated at $-78°C$ with 2.10 ml of a BuLi solution (3.36 mmol) and 20 min later with 5 ml of a water:Et_2O mixture (1:10). After workup as described for 3, a yield of 0.610 g (82%) is obtained. ^1H NMR: 4.02 ppm. ^{13}C NMR: 222.7 (MnCO), 86.3, 83.4, 83.2 (C_5) ppm.

5.3. Tricarbonyl(1,3-dibromocyclopentadienyl)manganese (5a)

0.43 g of 4a (0.97 mmol) are dissolved in 10 ml of Et_2O and treated with 0.61 ml of a BuLi solution (0.97 mmol) at $-78°C$. After 30 min, 5 ml of H_2O/Et_2O (1:10) is added, and the mixture warmed to room temperature within 15 min. After usual workup, 5a can be isolated in 0.16 g (yield 44%). ^1H NMR: 3.802 "d" (2H), 4.173 "t" (1H) (AB_2 multiplets). ^{13}C NMR: 223.4 (MnCO), 85.6, 83.4, 83.0 (C_5) ppm.

5.4. Tricarbonyl(bromocyclopentadienyl)manganese (6)

A solution of 0.14 g of 5a (0.38 mmol) in 5 ml of Et_2O is treated at $-78°C$ with 0.24 ml of a BuLi solution (0.38 mmol) and hydrolyzed 30 min later as usual. After standard workup, 6 can be isolated in low

yield (*ca.* 10%). ^1H NMR: 4.097 "t" (2H), 3.576 "t" (2H) (AA'XX' multiplets). ^{13}C NMR: 224.3 (MnCO), 85.0, 84.5, 81.4 (C_5) ppm.

5.5. Hydrolysis experiments

Standard procedure for the experiments from Tables 1 to 6:

100 mg of 1 or 2 are dissolved in the appropriate solvent and cooled down to the desired temperature by use of isopropanol-dry ice. The ^nBuLi is added by use of a micro- or milliliter syringe. Hydrolysis is performed by a large excess of MeOH. The solvents are evaporated *in vacuo*, with the temperature never exceeding $-45°C$. The residue is then extracted several times with a total volume of 50 ml pentane. After filtration through silicagel (2 cm × 0.5 cm) the solvent is removed in vacuo again, and the residue taken up in C_6D_6. The ^1H NMR spectra of these solutions (which had sometimes to be diluted further to get proper resolution) were integrated for the Cp–H signals to obtain the numerical values of product distribution.

Besides the NMR signals mentioned above, the remaining compounds were identified from the product mixtures:

4b: ^1H NMR: 3.77 ppm. **5b:** 3.915 "d" (2H), 3.421 "t" (1H) ppm (AB_2 multiplets). **7:** 3.865 ppm. **8:** 3.70 ppm. **9b:** 3.590 ppm.

5.6. Tricarbonyl(1,2,4-trichlorocyclopentadienyl)manganese (9a)

100 mg of 1 (0.238 mmol) are dissolved in 20 ml of THF and treated with 1.50 ml of a BuLi solution (2.4 mmol) at $-78°C$. After 5 min, 2 ml of MeOH are added quickly, and after another 5 min, the solvents are removed *in vacuo*. The pentane extract of the residue is then filtered through silicagel and evaporated to dryness. Yield 30 mg (41%). ^1H NMR: 3.870 ppm. ^{13}C NMR: 99.2, 98.5, 77.0 (C_5) ppm.

5.7. Control experiments

5.7.1. Entry 1

139 mg of 2 (0.33 mmol) are dissolved at $-78°C$ in 30 ml of hexane and treated with 0.20 ml of a BuLi solution (0.32 mmol). The white precipitate that formed is isolated by centrifugation and washed twice with a portion of 20 ml of pentane. The moist solid (2a) is treated with 20 ml of a THF solution of 50 mg of 1 (0.08 mmol) at $-78°C$, stirred for 20 min and hydrolyzed as usual.

5.7.2. Entry 2

300 mg of 1 (0.50 mmol), dissolved in 20 ml of Et_2O at $-70°C$, are treated with 6.4 ml of a BuLi solution

(10 mmol) and, after 3 min stirring, with 10 ml of cold methylcyclohexane. The ether is stripped off *in vacuo* immediately. The brown precipitate formed is isolated by centrifugation (< −50°C), washed with 5 ml of pentane, and then suspended in pentane and hydrolyzed by an excess of MeOH.

5.7.3. Entry 3

100 mg of **1** (0.167 mmol) and 52 mg of MeOH (1.7 mmol) are dissolved in 30 ml of THF and treated with 1.04 ml of a BuLi solution at −78°C. Solvents are evaporated *in vacuo*, with standard work-up procedure.

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