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METALATION OF DIBENZENECHROMIUM BY *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COMPLEXES OF n-BUTYLLITHIUM AND PHENYLLITHIUM

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SUMMARY

Dibenzenechromium is metalated by n-butyllithium in presence of TMEDA. The extent and orientation of metalation were investigated by mass spectrometric analysis of the products after quenching with D_2O. A lithium substituent on dibenzenechromium strongly activates the molecule for further metalation. Competition metalation of dibenzenechromium/benzene mixtures demonstrated the enhanced rate of metalation and therefore increased kinetic C–H acidity of the benzene molecule bound to chromium in a π-complex.

INTRODUCTION

The organic chemistry of dibenzenechromium (0) has so far been little studied. This is partly due to the restrictions placed by the ease of oxidation of dibenzenechromium(0) to the cationic species upon efforts to carry out substitution reactions on the benzene rings of the π-complex. As yet, the only known reaction of this type has been the metalation using suspensions of n-amylsodium in hexane, as reported by Fischer and Brunner[1]. Findings of Eberhardt and Butte[2] and Langer[3], demonstrating that n-alkyllithium reagents are dramatically activated if a tertiary diamine is added to chelate the lithium cation, prompted us to check whether this new metalation reaction could be used to lithiate dibenzenechromium*. n-Butyllithium itself was shown not to react with dibenzenechromium at all even after prolonged time of interaction[5]. The higher solubility and somewhat moderate reactivity of organolithium-compounds as compared to the sodium analogs, suggest, that lithiated dibenzenechromium might be a more versatile intermediate in the synthesis of functional derivatives.

RESULTS AND DISCUSSION

When dibenzenechromium was treated with the *N,N,N',N'*-tetramethylethylenediamine complex of n-butyllithium (TMEDA·n-BuLi) in cyclohexane at elevated temperature, transmetalation was effected as indicated by a colour change

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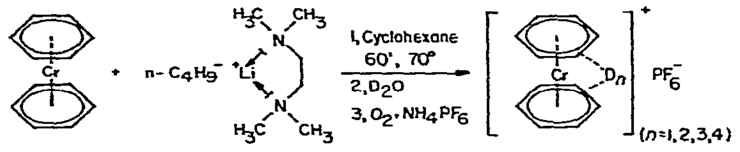
* During the course of our studies, Rausch *et al.*[4] reported the application of the TMEDA·n-BuLi reagent to the metalation of ferrocene.

of the solution from green-brown to red, and by the formation of a brown precipitate during later stages of the reaction. The extent of the transfer of lithium to dibenzenechromium was determined by quenching the reaction mixture with D_2O, oxidation of the partly deuterated neutral organometallic complex to the cation, and examination of its IR spectrum. Transmetalations using a molar ratio of TMEDA·n-BuLi to



dibenzenechromium of 5 : 1 yielded products, which after D_2O quenching showed an IR absorption at 2290 cm^{-1}, typical for the aromatic C–D stretching vibration. More detailed information concerning the extent of metalation and the formation of homo- and heteroannular disubstituted products was gained from mass spectrometric investigation, as summarized in Table 1. After correction for the abundance

TABLE 1

MASS SPECTRA OF PARTLY DEUTERATED DIBENZENECHROMIUM SAMPLES, OBTAINED FROM D_2O QUENCHING OF METALATION REACTION MIXTURES

A: $(C_6H_6)_2Cr$: n-BuLi·TMEDA 1 : 5, reaction time 60 min, 70°.
B: $(C_6H_6)_2Cr$: n-BuLi·TMEDA 1 : 5, reaction time 10 min, 70°.
C: $(C_6H_6)_2Cr$: n-BuLi·TMEDA 1 : 5, reaction time 60 min, 70°, deuterolysis of precipitate only.
D: $(C_6H_6)_2Cr$: PhLi·TMEDA 1 : 2, reaction time 16 h, 50°.

m/e		A	B	C	D
77	$C_6H_5^+$	16.5	23	15	20
78	$C_6H_6^+$	15	24	31	100
79	$C_5{}^{13}CH_6^+$, $C_6H_5D^+$	20	31	42	39
80	$C_6H_4D_2^+$	2	3	8.5	4
81				4	2
103	$CrC_4H_3^+$	3	3	2	4
104	$CrC_4H_4^+$	6	4	4	13
105	$CrC_4H_3D^+$, $^{53}CrC_4H_4^+$, $Cr^{13}CC_3H_4^+$	9	7	8	5
129	$CrC_6H_5^+$	8.5	8	7.5	9
130	$CrC_6H_6^+$	58	62	55	98
131	$CrC_6H_5D^+$, $Cr^{13}CC_5H_6^+$, $^{53}CrC_6H_6^+$	100	100	100	67
132	$CrC_6H_4D_2^+$, $^{54}CrC_6H_6^+$, $^{53}CrC_6H_5D^+$	21	20	30	15
133	$^{53}CrC_6H_4D_2^+$, $^{54}CrC_6H_5D^+$	5	5	10	2
206	$C_6H_5CrC_6H_5^+$	2	2	1	5
207	$C_6H_6CrC_6H_5^+$	2	2	2	3
208	$C_6H_6CrC_6H_6^+$	36	27	24	84
209	$C_6H_6CrC_6H_5D^+$, $C_6H_6Cr^{13}CC_5H_6^+$, $C_6H_6{}^{53}CrC_6H_6^+$	20	18	26	28
210	$C_6H_5DCrC_6H_5D^+$, $C_6H_6{}^{54}CrC_6H_6^+$, $C_6H_6{}^{53}CrC_6H_5D^+$	60	45	52	25
211	$C_6H_5DCrC_6H_4D_2^+$, $C_6H_6{}^{53}CrC_6H_4D_2^+$	16	12	19	9
212	$C_{12}H_8D_4Cr^+$	3.5	3	7.5	2

of heavy molecules due to the presence of ^{13}C, ^{53}Cr and ^{54}Cr, individual concentrations of the various deuterated dibenzenechromium molecules present in the samples could be calculated. The results, shown on a percentage basis, are listed in Table 2.

TABLE 2

YIELDS OF THE VARIOUS DEUTERATED SPECIES, CALCULATED FROM TABLE 1 (%)

	$C_{12}H_{12}Cr$	$C_{12}H_{11}DCr$	$C_{12}H_{10}D_2Cr$	$C_{12}H_9D_3Cr$	$C_{12}H_8D_4Cr$
A	33	11	52	2	2
B	33	14	50	2	1
C	24	20	45	7	4
D	72	6	18	3	1

The question of whether $C_{12}H_{10}D_2Cr$ represents homo- or heteroannular dimetalation can be answered by looking at the corrected intensities of the peaks of masses 80 ($C_6H_4D_2$) relative to 79 (C_6H_5D) and 132 ($C_6H_4D_2Cr$) relative to 131 (C_6H_5DCr), respectively. The small amounts of $C_6H_4D_2$ and $C_6H_4D_2Cr$ found in the mass spectra can be accounted for as stemming from fragmentation of $C_6H_5DCrC_6H_4D_2$, which implies, that virtually all the $C_{12}H_{10}D_2Cr$ peak represents heteroannular dimetalation. In order to decide whether clean mono- or dimetalation could be achieved under controlled conditions, the reaction was quenched at different stages. The fact that dimetalated dibenzenechromium formed the main product even at an early stage and even when n-butyllithium was replaced by the less reactive phenyllithium demonstrates that lithium as a substituent on dibenzenechromium strongly activates the molecule for further metalation.

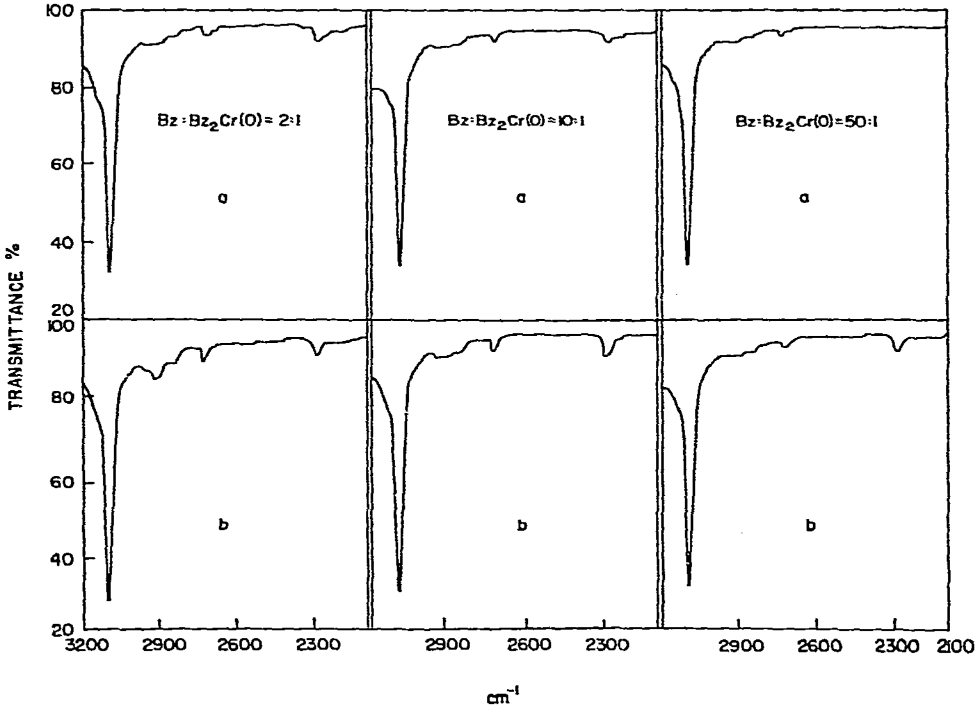


Fig. 1. IR spectra of $(C_{12}H_{12-n}D_nCr)PF_6$ samples, obtained after D_2O quenching of competition metalation reaction mixtures; (a) free benzene added in the molar ratio as indicated; (b) blanks, run under analogous conditions, no benzene added.

With the intention of studying the effect π-bonded chromium exerts upon the reactivity of the benzene nucleus towards the metalating reagent, competition experiments were carried out in which free benzene was added to the reaction mixture in varying amounts. If free and π-bonded benzene were present in a 1 : 1 ratio, the yield of metalated dibenzenechromium remained virtually unchanged, free benzene in 5-fold excess slightly decreased the extent of metalation of π-bonded benzene and only when free benzene was present in a 25-fold excess was metalation of dibenzenechromium suppressed completely, as inferred from the intensities of the IR absorption at 2290 cm^{-1} (Fig. 1).

Further evidence in support of the conclusion that benzene π-bonded to chromium is metalated preferentially to free benzene could be obtained from NMR measurements in form of the relative rate if the competition metalation was carried out in a NMR sample tube and the spectra were recorded in short intervals. Metalation of ring positions involves a decrease in intensity of the single sharp signal of dibenzenechromium ($\tau = 5.96$) and benzene ($\tau = 3.02$), respectively. Instead, the metalated benzene rings show unresolved multiplets. Since the sharp signal of remaining unmetalated material is superimposed upon the broad multiplet which gradually builds up during the transmetalation reaction, a comparison of signal area decrease (benzene protons *versus* dibenzenechromium protons) only yields a minimum value for the rate enhancement of dibenzenechromium relative to benzene. From the NMR

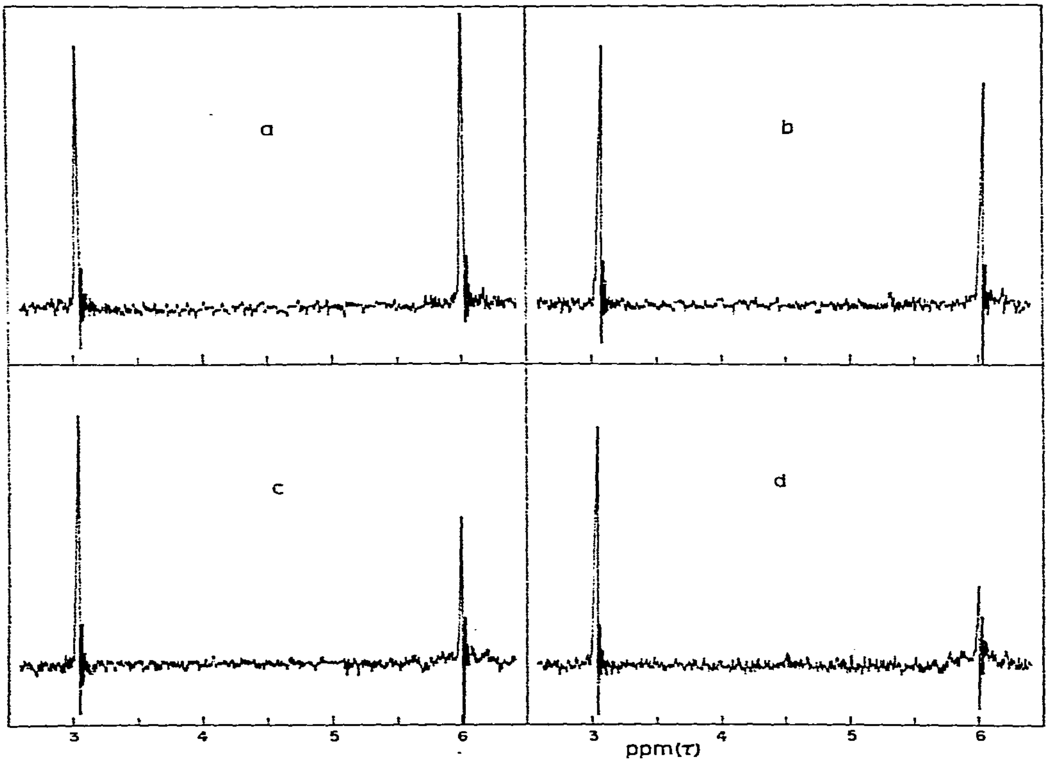
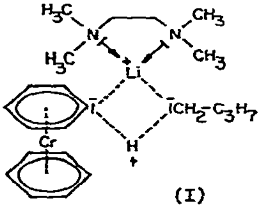


Fig. 2. ^1H NMR spectra of competition metalation reaction mixture, recorded at different reaction times: (a) after 5 min; (b) after 12 min; (c) after 25 min; (d) after 80 min. Reaction temperature 60°.

spectra (Fig. 2) a factor of about 10 can be derived for the relative rate of metalation of dibenzenechromium as compared to benzene (relative rate = 1).

This appreciable enhancement of the rate of metalation implies an increased kinetic C–H acidity of benzene, bound to chromium in a π-complex. Although the detailed mechanism of metal/hydrogen exchange reactions is unknown at present[6], there seems to be general agreement that the rate determining step in metalation reactions is abstraction of a proton from the carbon atom to be metalated by the attack of a strong base[7], which in the example under investigation would be the n-butyl carbanion of the n-BuLi·TMEDA complex.



(I)

Therefore, the dibenzenechromium component of transition state (I) will to a certain extent assume carbanion character and the observed rate increase should be explained in terms of extra stabilization of the dibenzenechromium carbanion as compared to the benzene carbanion. Since the orbital occupied by the electron pair which formed the bond between ring carbon atom and the leaving proton is orthogonal to the π-orbitals of the benzene nucleus, no simple stabilization by delocalization of this electron pair over the whole π-electron system is conceivable. Typically, the kinetic C–H acidity of substituted benzene derivatives is influenced predominantly by inductive effects, resonance effects playing a minor role if they have to be considered at all[8,9]. In the transition state of the metalation of dibenzenechromium a type of carbanion stabilization by metal participation therefore seems plausible, in which the orbital, containing the electron pair of the C–H bond being broken, interacts with an empty antibonding orbital of suitable symmetry centered on chromium. The influence of *d*-orbital participation of a neighboring atom on C–H acidity is well established [*e.g.* relative rates of proton exchange of $(CH_3)_4N^+ : (CH_3)_4P^+ : (CH_3)_3$-$S^+ = 1 : 2.4 \times 10^6 : 2 \times 10^7$ [10]].

The applicability of the new lithiation reaction to the synthesis of functional derivatives of dibenzenechromium is currently being tested.

EXPERIMENTAL

Unless mentioned otherwise, all work was performed under an atmosphere of dry nitrogen free of oxygen. Dibenzenechromium was obtained from the reducing Friedel–Crafts synthesis. n-Butyllithium was prepared in cyclohexane and used after filtration as a 0.75 molar solution. *N,N,N′,N′*-Tetramethylethylenediamine (Fluka AG) was used without further purification. Solvents were distilled from calcium hydride.

Metalation of dibenzenechromium

In a small Schlenk tube were placed 2.5 mmoles (3.3 ml of the 0.75 molar stock solution) of n-butyllithium and 8 ml of cyclohexane. Addition of 0.35 ml (2.5 mmoles) of TMEDA caused a change from colourless to pale yellow. 104 mg (0.5 mmole) of powdered dibenzenechromium were then added and the mixture was heated with stirring to 70° for 60 min. After cooling to room temperature the reaction mixture was quenched with 3 ml of D_2O and air was bubbled through the two phase system until the cyclohexane phase had become colourless. From the yellow aqueous solution the partially deuterated dibenzenechromium-cation was precipitated with aqueous ammonium hexafluorophosphate. After washing with water, ethanol, ether and drying in vacuo, the IR spectra of the salt were recorded in KBr.

Mass spectrometric analysis

The metalation was stopped after 10 min at 70° when the colour changed from brown to red but no precipitate had yet formed. The red solution was deuterolysed, 0.1 g of sodium dithionate and 0.1 g of sodium hydroxide were added and the mixture was stirred at room temperature for 20 min. The cyclohexane layer was evaporated to dryness and deuterated dibenzenechromium was obtained from sublimation of the residue (120°, HV). In another preparation, the metalation was allowed to proceed for 60 min at 70° but the reaction mixture was then filtered and only the brown precipitate was deuterolysed and worked up. In the metalation using phenyllithium instead of n-butyllithium, the reaction mixture was stirred for 16 h at 50°. The mass spectra of the products were obtained from an Atlas CH 4 mass spectrometer operating at 70 eV ionizing voltage.

Competition metalation of dibenzenechromium/benzene mixtures

Reactions were carried out as described but in addition to 104 mg (0.5 mmole) dibenzenechromium there were added 39 mg (0.5 mmole), 390 mg (5 mmoles) and 1.95 g (25 mmoles) of benzene, respectively. With every competition metalation was run a blank where benzene was replaced by an equivalent amount of cyclohexane. IR spectra were recorded after D_2O quenching as described above. ^1H NMR measurements were carried out on a Varian A-60 NMR spectrometer. A cyclohexane solution was prepared which was 0.041 molar in dibenzenechromium, 0.082 molar in benzene and 0.205 molar in n-butyllithium. An amount of TMEDA, equivalent to n-butyllithium present, was added and the mixture was rapidly transferred to a NMR sample tube which was sealed under N_2 and maintained at a temperature of 60° during NMR measurement.

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