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Nucleophilic Substitution Reactions in Fluorinated Bis(arene)chromium Complexes[1]

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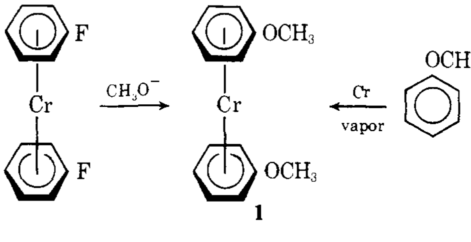
Abstract: Fluorinated bis(arene)chromium complexes undergo nucleophilic substitution reactions, with loss of fluoride, under very mild conditions in an analogous fashion to hexafluorobenzene. Thus, bis(η-fluorobenzene)chromium reacts with sodium methoxide to yield bis(η-methoxybenzene)chromium. (η-Benzene)(η-hexafluorobenzene)chromium (**2**) reacts with alkyl or aryl lithium reagents at −78° to give polysubstituted products. Furthermore, *tert*-butyllithium abstracts a proton from the π-complexed C_6H_6 ring in **2** to generate a new nucleophile which attacks **2** to yield **6**, which has a bridging pentafluorobiphenyl group.

The chemistry of bis(arene)chromium complexes has hitherto been restricted to metalation reactions[2-4] and base-catalyzed hydrogen-deuterium exchange processes.[5,6] Electrophilic or free radical attack on the complexed arene rings is unlikely owing to the presence of the relatively electron-rich chromium atom which provides a much more attractive target for an incoming electrophile. Conversely, nucleophilic attack on the complexed rings should be enhanced relative to the free arene, and indeed in the corresponding arene-chromium tricarbonyl systems synthetic schemes have been based on this premise.[7]

However, nucleophilic displacement requires the presence of a suitable leaving group, and such systems cannot be synthesized by the route pioneered by Fischer and Hafner,[8] since arenes possessing substituents with nonbonded electron pairs react with the Lewis acid catalyst ($AlCl_3$) thus preventing formation of sandwich complexes. Fortunately the recently developed metal atom cocondensation technique[9,10] provides a viable synthetic route by which leaving groups (e.g., halogens) can be incorporated into chromium-arene sandwich compounds.[11-14]

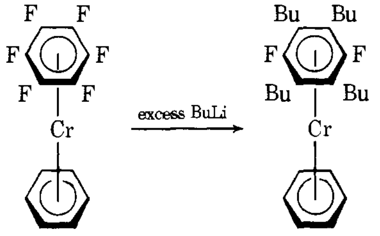
Results and Discussion

^{19}F NMR studies on a series of fluoro-substituted bis(arene)chromium complexes indicated that a π-complexed chromium atom has a similar effect on an aromatic ring as do four ring fluorine atoms.[13] Thus, bis(η-1,4-difluorobenzene)chromium would be expected to undergo nucleophilic substitution with loss of fluoride ion in an analogous fashion to the known chemistry of hexafluorobenzene.[15] Preliminary experiments with bis(η-fluorobenzene)chromium and sodium methoxide led to a very low yield of bis(η-methoxybenzene)chromium (**1**), which was identified by comparison of its mass spectrum and proton NMR spectrum with that of an authentic sample made by the direct reaction of anisole with chromium atoms. However, the reported synthesis by Timms[12] of (η-benzene)(η-hexafluorobenzene)chromium (**2**) by the cocondensation procedure provided an ideal system in which nucleophilic substitution could occur in only one ring. Hexafluorobenzene complexes of other metals have been reported, but they are of low thermal stability.[16] Although hexafluorobenzene reacts with sodium methoxide or piperidine at moderate temperatures,[15] no appreciable reaction with **2** was observed even after several hours reflux at 60°. Butyllithium is reported to react with C_6F_6 at −78° to produce a mixture of mono-, di-, tri-, and tetrasubstituted products, whereas *tert*-butyllithium yields only the mono- and disubstituted arenes.[17]



1

Accordingly, a 5 molar excess of n-butyllithium and **2** were mixed in ether at −78° and upon warm-up the major product isolated was the tetrasubstituted derivative **3**. The product was identified by its mass spectrum (see Table I) which showed the parent ion and loss of fluorines and alkyl groups. The major fragmentation route in this case, as with many others we have studied, involves cleavage of the fluoroarene-chromium bond with loss of C_6H_6-Cr (m/e 130) and subsequent breakdown of the substituted ring. The ^{19}F NMR of **3** in deuteriobenzene shows a single peak at 180.2 ppm to high field of $CFCl_3$, suggesting the para isomer; this assignment is reinforced by the observation that the spectrum 24 h later (the solution having changed from red to green due to decomposition of the complex) showed a peak at 126.7 ppm, while the free arene, 1,2,4,5-tetrakis(n-butyl)-3,6-difluorobenzene, is reported to absorb at 127.2



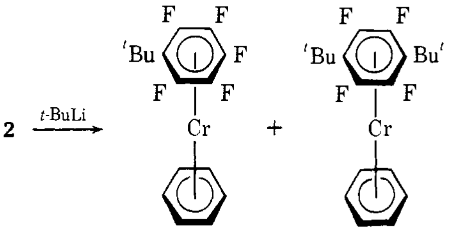
2 **3**

Table I. Mass Spectral Data for Substituted Chromarenes

m/e	Assignment	Rel int
	$(C_6H_5OCH_3)_2Cr$ (**1**)	
268	$C_{14}H_{16}O_2Cr^+$	64.4
253	$C_{13}H_{13}O_2Cr^+$	0.3
237	$C_{13}H_{13}OCr^+$	0.7
160	$C_7H_8OCr^+$	85.4
145	$C_6H_5OCr^+$	32.2
129	$C_6H_5Cr^+$	3.7
108	$C_7H_8O^+$	38.5
93	$C_6H_5O^+$	8.1
77	$C_6H_5^+$	100
	$(C_6H_6)Cr(C_6F_6)$ (**2**)	
316	$C_{12}H_6F_6Cr^+$	3.0
297	$C_2H_6F_5Cr^+$	0.7
278	$C_{12}H_6F_4Cr^+$	0.3
186	$C_6F_6^+$	1.1
168	$C_6HF_5^+$	15.7
150	$C_6H_2F_4^+$	1.8
149	$C_6HF_4^+$	1.8
148	$C_6F_4^+$	0.8
137	$C_5HF_4^+$	1.7
100	$C_2F_4^+$	3.6
78	$C_6H_6^+$	100
	$(C_6H_6)Cr(C_6Bu_4F_2)$ (**3**)	
468	$C_{28}H_{42}F_2Cr^+$	0.3
449	$C_{28}H_{42}FCr^+$	0.6
430	$C_{28}H_{42}Cr^+$	0.1
338	$C_{22}H_{36}F_2^+$	0.5
319	$C_{22}H_{36}F^+$	0.2
300	$C_{22}H_{36}^+$	22.8
282	$C_{18}H_{28}F_2^+$	7.1
262	$C_{18}H_{27}F^+$	4.9
257	$C_{19}H_{29}^+$	60.8
244	$C_{18}H_{28}^+$	6.3
226	$C_{14}H_{20}F_2^+$	3.4
207	$C_{14}H_{20}F^+$	4.0
151	$C_{10}H_{12}F^+$	6.1
133	$C_{10}H_{13}^+$	5.7
127	$C_{10}H_7^+$	7.2
95	$C_6H_4F^+$	4.6
91	$C_7H_7^+$	3.2
78	$C_6H_6^+$	100
	$(C_6H_6)Cr(C_6F_5Bu^t)$ (**4**)	
354	$C_{16}H_{15}F_5Cr^+$	0.5
339	$C_{15}H_{12}F_5Cr^+$	0.9
311	$C_{13}H_8F_5Cr^+$	1.0
298	$C_{12}H_7F_5Cr^+$	4.1
224	$C_{10}H_9F_5^+$	2.9
209	$C_9H_6F_5^+$	9.9
181	$C_7H_2F_5^+$	18.8
168	$C_6HF_5^+$	26.4
149	$C_6HF_4^+$	3.1
130	$C_6H_6Cr^+$	3.6
78	$C_6H_6^+$	100
	$(C_6H_6)Cr(C_6F_4Bu_2^t)$ (**5**)	
392	$C_{20}H_{24}F_4Cr^+$	0.5
377	$C_{19}H_{21}F_4Cr^+$	1.6
364	$C_{18}H_{20}F_4Cr^+$	0.4
349	$C_{17}H_{17}F_4Cr^+$	0.7
336	$C_{16}H_{16}F_4Cr^+$	0.4
321	$C_{15}H_{13}F_4Cr^+$	0.7
262	$C_{14}H_{18}F_4^+$	2.0
247	$C_{13}H_{15}F_4^+$	4.0
234	$C_{12}H_{14}F_4^+$	5.3
219	$C_{11}H_{11}F_4^+$	4.1
206	$C_{10}H_{10}F_4^+$	5.7
191	$C_9H_7F_4^+$	23.1
150	$C_6H_2F_4^+$	6.9
130	$C_6H_6Cr^+$	3.8
78	$C_6H_6^+$	100
57	$C_4H_9^+$	65.9
	$(C_6F_6)Cr(C_6H_5 \cdot C_6F_5)Cr(C_6H_6)$ (**6**)	
482	$C_{18}H_5F_{11}Cr^+$	0.7
463	$C_{18}H_5F_{10}Cr^+$	2.5
444	$C_{18}H_5F_9Cr^+$	1.7
426	$C_{18}H_{11}F_5Cr_2^+$	0.6
374	$C_{18}H_{11}F_5Cr^+$	0.2
297	$C_{12}H_6F_5Cr^+$	0.6
244	$C_{12}H_5F_5^+$	0.8
186	$C_6F_6^+$	8.6
167	$C_6F_5^+$	1.9
130	$C_6H_6Cr^+$	3.8
78	$C_6H_6^+$	100
	$(C_6H_6)Cr(C_6F_5 \cdot C_6H_5)$ (**8**)	
374	$C_{18}H_{11}F_5Cr^+$	30.0
336	$C_{18}H_{11}F_3Cr^+$	8.8
334	$C_{15}H_7F_5Cr^+$	9.1
322	$C_{14}H_7F_5Cr^+$	13.2
244	$C_{12}H_5F_5^+$	20.0
225	$C_{12}H_5F_4^+$	8.5
206	$C_{12}H_5F_3^+$	12.1
193	$C_{11}H_4F_3^+$	12.1
167	$C_6F_5^+$	10.9
149	$C_6H_6FCr^+$	13.9
130	$C_6H_6Cr^+$	77.4
95	$C_6H_4F^+$	100
91	$C_7H_7^+$	74.2

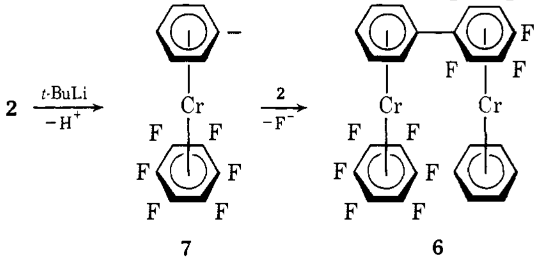
ppm in CCl_4 solution.[17] This reaction parallels the chemistry of the free arene except that there are only trace quantities of the less substituted products. Gilman's rationale[17] that the substitution stops at four due to a combination of electronic and steric factors is clearly applicable here.

In contrast, *tert*-butyllithium shows little propensity for substitution giving rise to low yields of the mono- and disubstituted chromium complexes, **4** and **5**, for which mass spectral data are listed in Table I. This may well be sterically controlled, and by analogy to the free arene the disubstituted product is presumed (but not definitely proven!) to be the para isomer.



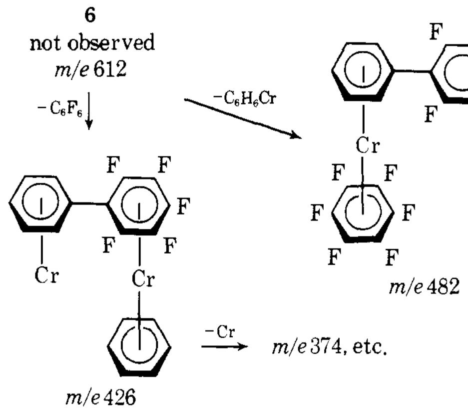
4 **5**

An unexpected product, **6**, from this reaction was readily rationalizable after the fact. This showed large mass spectral peaks at *m/e* 482, 426, and 374 as well as the usual lower mass peaks due to breakdown of the rings. We suggest that the bulky and strongly basic *tert*-butyl carbanion undergoes nucleophilic substitutions only with some difficulty on the relatively hindered C_6F_6 ring, and so a competing reaction is proton abstraction from the π-complexed C_6H_6 ring to generate the organometallic carbanion **7** which itself is capable of nucleophilic attack on another molecule of **2**. The low yields and tarry residue may be at-



7 **6**

Scheme I



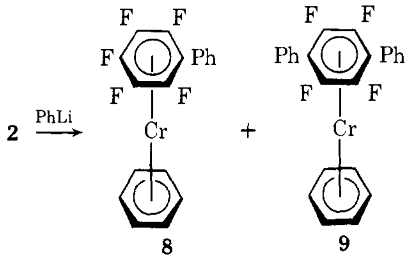
tributable to further proton abstraction from **6** leading eventually to polymer formation.

The mass spectral data are thus readily rationalizable by the indicated cleavages, as can be seen in Scheme I.

The acidity of the protons of the π-complexed C_6H_6 ring is not surprising in view of the known ability of relatively weak bases to catalyze H/D exchange in the $(C_6H_6)_2Cr^+$ systems.[5] In **2** there is presumably a drift of electron density from the chromium to the C_6F_6 ring which tends to increase the acidity of the protons in the other ring. Furthermore, the carbanion **7** would be stabilized by delocalization of the charge via the chromium onto the C_6F_6 ring. There is clearly electronic interaction between the two rings as evidenced by the ^{19}F and ^1H NMR spectra of **2** in which each appears as 1:6:15:20:15:6:1 septets (see Figure 1).

The "internal oxidation" of the chromium atom in **2** is also compatible with its surprisingly high air stability, and supports Klabunde's assertion[14] that electron-withdrawing arenes would retard the one-electron oxidation of chromium and thus enhance the stability of the complex. The implication that the chromium is somewhat electron deficient to be regarded as Cr(0) and that the C_6F_6 ring is thus more electron rich than the free ligand is supported by ESCA data which show that there is less difference in the C_{1s} binding energies between the complexed C_6F_6 and C_6H_6 rings than in the free ligands.[18] One might thus be tempted to postulate that the C_6F_6 ring would be less susceptible than the free ligand to nucleophilic attack. The experimental evidence is equivocal on this point. Although piperidine and sodium methoxide do not attack the complex under mild conditions which bring about reactions with C_6F_6, in contrast excess *n*-butyllithium gives directly the tetrasubstituted product with only traces of the mono-, di-, or trisubstituted complexes. Clearly there are mechanistic depths which still have to be plumbed!

A clean monosubstitution reaction was finally achieved by treating **2** with phenyllithium at −78°. The yellow solution turned orange, and removal of the solvent and sublimation of the residue yielded deep orange **8**, identified by its mass spectrum and NMR. A very small amount of the disubstituted complex **9** was also obtained and identified mass spectroscopically.



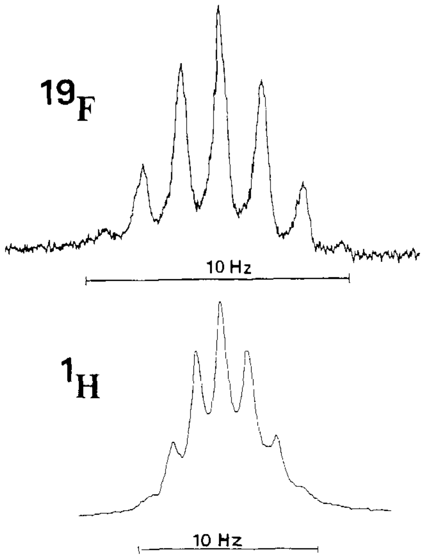


Figure 1. The ^{19}F and ^1H NMR spectra of (η-benzene)(η-hexafluorobenzene)chromium (**2**).

There is no doubt that the chromium is complexed to the fluorinated ring of the biphenyl system in **8** since the ^{19}F NMR chemical shifts are much too high to be attributed to a noncomplexed pentafluorophenyl system. ^{19}F NMR absorptions of all previously reported π-bonded fluoroarene–chromium complexes exhibit large upfield shifts. Thus fluoroarene–chromium tricarbonyls show upfield shifts of ca. 20 ppm relative to the free arenes.[12,19,20] In symmetrically substituted bis(η-fluoroarene)chromium compounds a 40-ppm upfield shift is typical;[13] **2** absorbs at 30.4 ppm upfield of C_6F_6. In **8** we assign the lowest field multiplet (basically a doublet of doublets) to the ortho fluorines and the complex multiplet at 194.5 ppm to the meta fluorines. The 196.6 ppm complex triplet is unambiguously assignable to the single para fluorine atom on the basis of intensity alone. Thus, the ortho, meta, and para fluorines show upfield shifts of 37.8, 31.5, and 39.9 ppm, respectively, relative to the free arene. These assignments are also consistent with those for (η-benzene)(η-pentafluorobenzene)chromium where the assignments are definitive due to coupling to the unique hydrogen atom.[21] Furthermore, the ^1H spectrum of **8** shows multiplets at δ 7.78 (5 H) and 4.58 (6 H) indicating the presence of a noncomplexed phenyl system and a π-complexed benzene ring. It was not possible to resolve completely the multiplicity of the peak attributable to the π-bonded ring, but apparently it couples to the fluorine atoms in the other ring in an analogous manner to **2**.

The ^{13}C NMR spectrum of **2** provides an interesting comparison between the two complexed rings and also between the sandwich compound and benzene–chromium tricarbonyl. Thus C_6H_6 absorbs at 128 ppm (downfield of Me_4Si) and $^1J_{C-H}$ is 158 Hz. Upon complexation to a chromium tricarbonyl moiety an upfield shift of 33 ppm is observed; $^1J_{C-H}$ increases to 173 Hz and this increase has been the subject of some discussion.[22,23] Hexafluorobenzene–chromium tricarbonyl has not yet been synthesized, although $(C_6F_6)Cr(PF_3)_3$ is known[12] but its ^{13}C spectrum has not been published. ^{13}C spectra of bis(arene)chromiums have been discussed[24] but, to the best of our knowledge, these data are not yet available in the literature.

In the case of $(C_6F_6)Cr(C_6H_6)$ we observe upfield shifts relative to the free arenes for both rings, the C_6H_6 ring by 43 ppm and the C_6F_6 ring by 16 ppm. Furthermore, the coupling constants change quite markedly. Thus $^1J_{C-H}$ is 170.9 Hz (measured by gated decoupling of the ^{13}C spectrum and by the ^{13}C satellites in the ^1H spectrum) and closely parallels the benzene-chromium tricarbonyl case.[22,23] $^1J_{C\text{-}F}$ is now 303 Hz (cf. 362 Hz in C_6F_6[25]), but this change is not amenable to a simple explanation.[26] These data may be compared with the ^{19}F NMR of bis(η-fluoroarene)chromiums and fluoroarene-chromium tricarbonyls where large upfield shifts and decreased H–F coupling constants are the rule.[13,20]

However, these data are at variance with the somewhat simplistic ideas advanced recently whereby ^{13}C chemical shifts are correlated solely with π-electron density. Thus, benzene-chromium tricarbonyl is predicted[27] to be $[C_6H_6]^{0.92-}Cr(CO)_3{}^{0.92+}$, thus implying high susceptibility of the ring to electrophilic attack whereas the reverse is actually true.[28] Furthermore, in **2** the C_6H_6 ring is clearly electron-depleted relative to the C_6F_6 ring and yet is 37 ppm further upfield! Apparently, the recent cautionary comments[29] with regard to ^{13}C data on organometallic systems are justified.

Experimental Section

^1H and ^{19}F nuclear magnetic resonance spectra were recorded on a Varian DP-60 spectrometer as solutions in perdeuteriobenzene using Me_4Si and $CFCl_3$ as internal standards. ^{13}C spectra were recorded on a Bruker WH-90 instrument operating at 22.63 MHz using $CDCl_3$ as solvent and Me_4Si as the internal reference. Mass spectra were recorded on a C.E.C. 21-110-B spectrometer operating at 70 eV with an inlet temperature of 140 °C. Melting points are uncorrected. Elemental analyses were performed by Gygli Microanalysis Laboratory, Toronto.

Bis(η-fluorobenzene)chromium. Bis(η-fluorobenzene)chromium was prepared by the reaction of atomic chromium vapor with fluorobenzene using the cocondensation procedure fully described elsewhere.[11]

1,1′-Dimethoxychromarene (1). (a) Chromium vapor (350 mg, 6.73 mmol) and anisole (25 g, 231.5 mmol) were cocondensed at −196 °C, in the apparatus previously described,[13] over a 50-min period. The reaction flask was allowed to warm to room temperature, the excess unreacted anisole removed under vacuum, and the product sublimed to the water-cooled upper portion of the flask. The apparatus was flushed repeatedly with dry nitrogen and then the removable reaction flask was rapidly transferred to a large glovebag for removal and subsequent sublimation of the brown, highly air-sensitive bis(η-methoxybenzene)chromium (**1**), (198 mg, 0.74 mmol; 11%). The ^1H NMR spectrum shows a multiplet (5 H) from δ 5.75 to 5.9 and a singlet (3 H) at δ 3.25. These values compare favorably with those for the previously reported Mo and W analogues.[30] The mass spectral data are collected in Table I.

(b) Bis(η-fluorobenzene)chromium (103 mg, 0.42 mmol) and sodium methoxide (1.35 g, 25.0 mmol) in dry methanol (250 ml) were stirred at 40–45 °C for 14 h under a nitrogen atmosphere. Removal of solvent under vacuum and sublimation of the residue produced bis(η-methoxybenzene)chromium (9.0 mg, 0.034 mmol; 8%), identified by comparison of its NMR and mass spectra with those of the independently synthesized sample.

(η-Benzene)(η-hexafluorobenzene)chromium (2). Chromium vapor (132 mg, 2.54 mmol) and 25 ml of a 60/40 v/v mixture of hexafluorobenzene and benzene were cocondensed as previously described, and the resulting matrix was allowed to melt and gradually attain ambient temperature. The lower portion of the flask was surrounded by a 60 °C water bath while the upper part of the flask was encircled by several coils of water-cooled Tygon tubing. A yellowish-green mixture of bis(η-benzene)chromium and (η-benzene)(η-hexafluorobenzene)chromium[31] was removed from the upper portion of the flask and left in air overnight to effect a differential oxidation. [$(C_6H_6)_2Cr$ is air unstable, while the desired product, **2**, is stable not only in air for several weeks but even in benzene or ether solution for several days.] Subsequent sublimation gave crude yellow **2** which was recrystallized from diethyl ether-benzene to give lustrous yellow needles (68 mg, 0.22 mmol; 8.5%), mp 139°. The ^1H NMR spectrum shows a septet (J = 1.43 Hz) at δ 4.50; ^{19}F NMR shows a septet (J = 1.44 Hz) at 193.3 ppm upfield of $CFCl_3$; ^{13}C NMR (proton decoupled) shows a doublet ($^1J_{C\text{-}F}$ = 3.03 Hz) at 121.7 ppm and a singlet at 85.8 ppm downfield of Me_4Si. The mass spectral data are collected in Table I.

Anal. Calcd for $C_{12}H_6CrF_6$: C, 45.6; H, 1.9. Found: C, 45.6; H, 1.6.

Nucleophilic Substitution Reactions on 2. (a) **Sodium methoxide** (8.7 mg, 0.16 mmol) in 20 ml dry methanol was added to **2** (50.6 mg, 0.16 mmol) in dibutyl ether (20 ml), and the mixture stirred under nitrogen at 70° for 14 h. NMR examination of the solution indicated the presence of starting materials only.

(b) **Piperidine** (100 mg, 1.18 mmol) and **2** (32 mg, 0.10 mmol) in diethyl ether (15 ml) were stirred at 40° under nitrogen for 14 h, but NMR investigation showed that no reaction had occurred. Addition of dibutyl ether (25 ml) to the mixture and subsequent stirring at 85° for 3 h produced a color change from yellow to brown. Although the solution gave a positive test for fluoride ion, NMR failed to detect any new compounds.

(c) ***n*-Butyllithium** (35.8 mg, 0.56 mmol) in diethyl ether (25 ml) was added dropwise to a solution of **2** (36 mg, 0.11 mmol) in 15 ml of ether at −78° under nitrogen. After 90 min the solution was gradually allowed to warm to room temperature. The now orange solution was stirred for 10 h, the lithium fluoride filtered off, the solvent removed under vacuum, and the red residue was examined by NMR and mass spectrometry. ^{19}F NMR revealed peaks at 126.7 and 180.1 ppm to high field of $CFCl_3$. After 24 h the red solution had turned green and the peak at 126.7 ppm had increased about fourfold at the expense of the high-field peak. The mass spectral data for (η-benzene)(η-1,2,4,5-tetrabutyl-3,6-difluorobenzene)chromium are presented in Table I.

(d) ***tert*-Butyllithium** (45.2 mg, 0.71 mmol) in diethyl ether (100 ml) was added dropwise to a solution of **2** (98 mg, 0.31 mmol) in ether (50 ml) at −78° under nitrogen. The solution was slowly allowed to warm to room temperature and stirred for a further 2 h. After filtration and removal of solvent under vacuum, the residue was sublimed to give a very low yield (<1%) of an orange-red oil. Although it was not possible to separate clearly the components of this oil chromatographically, their volatilities were such that fractional sublimation enabled one to obtain three samples whose mass spectra contained only very minor contaminants. They were identified as (η-benzene)(η-1-*tert*-butyl-2,3,4,5,6-pentafluorobenzene)chromium (**4**), (η-benzene)(η-1,4-di-*tert*-butyl-2,3,5,6-tetrafluorobenzene)chromium (**5**), and the complex **6**, which has a bridging pentafluorobiphenyl group.[32] The mass spectra of **4**, **5**, and **6** are presented in Table I. In all cases chromium-containing ions exhibited the correct isotopic abundance pattern; furthermore, several of the fragmentation routes are supported by appropriate metastable peaks.

(e) **Phenyllithium** (25.2 mg, 0.3 mmol) in ether (100 ml) was added dropwise to **2** (63 mg, 0.2 mmol) in ether (50 ml) at −78° temperature and stirred for another 2 h, the solution was filtered to remove lithium fluoride and the solvent was removed under vacuum. The residue was sublimed at 60° (2 mm) to yield red microcrystals of (η-benzene)[1′-6′-η-(2,3,4,5,6-pentafluoro-1,1′-biphenyl)]chromium (**8**) (18 mg, 0.048 mmol; 24%), mp 130°. The ^1H NMR shows a narrow multiplet (6 H) at δ 4.58 and a multiplet (5 H) centered at δ 7.7. The ^{19}F NMR shows three multiplets at 181.9 (2 F), 194.5 (2 F), and 196.6 (1 F) ppm to high field of $CFCl_3$. The mass spectral data are presented in Table I.

Anal. Calcd for $C_{18}H_{11}CrF_5$: C, 57.7; H, 2.9. Found: C, 57.8; H, 2.8.

The mass spectrum of the residue remaining after sublimation of **8** showed peaks at m/e 432, 354, and 302 (parent ion, P − C_6H_6 and P − C_6H_6Cr) which are assignable to the diphenyl-substituted complex whose structure is probably **9**.

Acknowledgments. We thank the National Research Council of Canada and the McMaster University Science and Engineering Research Board for financial support, and J. I. A. Thompson and B. G. Sayer for the ^{19}F and ^{13}C NMR spectra.

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Mechanism of the Sodium Cyanoborohydride Reduction of α,β-Unsaturated Tosylhydrazones

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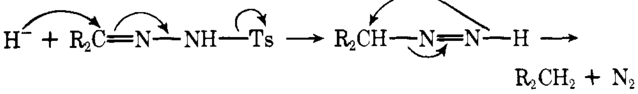
Received September 9, 1975

Abstract: Through the use of several steroidal cisoid and transoid α,β-unsaturated tosylhydrazones, it has been possible to establish the course of the $NaBH_3CN$ reduction of such tosylhydrazones. Depending on the nature of the tosylhydrazone, alkane, or alkene (with double bond migration to the site of the carbonyl carbon) or both may be formed. Alkene formation is initiated by hydride reduction of the imminium system, while alkanes are produced by initial Michael-type addition of hydride to the terminus of the conjugated system followed by reduction of the imminium moiety. Supporting evidence is provided by the course of $NaBD_3CN$ reductions and demonstration that in alkene products deuterium is attached to the carbon which bore the original carbonyl group.

Sodium cyanoborohydride ($NaBH_3CN$) has recently been shown to be a mild, highly selective reagent[1] for the reduction of tosylhydrazone derivatives of aliphatic ketones and aldehydes.[2] As such, this reaction provides a convenient alternative to the Wolff-Kishner and Clemmensen reductions and other direct or indirect deoxygenation methods.[3] It has also been reported that the $NaBH_3CN$ reduction of α,β-unsaturated tosylhydrazones cleanly produces the alkene resulting from migration of the double bond to the carbon originally bearing the carbonyl group.[2b] This result is in contrast to the observation of Caglioti and Magi[4] that the lithium aluminum hydride reduction of α,β-unsaturated tosylhydrazones leads to the formation of mixtures of hydrocarbons. In light of these reports and since the labeled reagent sodium cyanoborodeuteride ($NaBD_3CN$) can be readily prepared by exchanging the hydrogens of $NaBH_3CN$ for deuterium,[1b,c] it was decided to investigate the mechanism of the tosylhydrazone reduction with $NaBH_3CN$ and to determine the feasibility of this procedure for selective deuterium labeling.

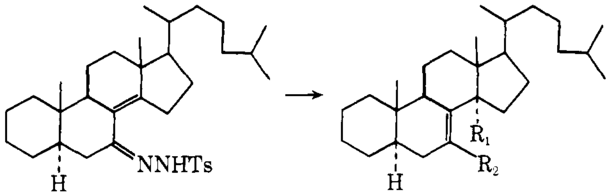
In particular, as part of our continuing effort to synthesize deuterium-labeled steroids for mass spectrometric studies, it was necessary to synthesize 12,12-d_2 steroid hydrocarbons from the corresponding ketones in high chemical and isotopic yields.[5] When the tosylhydrazones of 3- or 12-keto steroids were reduced with $NaBH_3CN$, it was found that pure hydrocarbon product was formed in yields of 75–90%. Use of D_2O in the work-up procedure gave unlabeled product, whereas $NaBD_3CN$ as the reducing agent generated a singly deuterated hydrocarbon. A d_2-labeled compound was obtained by deuterium exchange of the hydrogen on the nitrogen of the tosylhydrazone and reduction with $NaBD_3CN$ using deuterated acid catalyst.[6] Therefore, the reduction of saturated tosylhydrazones proceeds operationally and mechanistically in the same fashion as had been demonstrated earlier by us[7] for sodium borohydride (Scheme I).

Scheme I



$$H^- + R_2C{=}N{-}NH{-}Ts \longrightarrow R_2CH{-}N{=}N{-}H \longrightarrow R_2CH_2 + N_2$$

In connection with another project, we needed to synthesize the labeled alkene cholest-7-ene-*14α-d*$_1$ (**2a**). According to the findings of Hutchins and co-workers[2b] 14α-cholest-7-ene (**2b**) should be cleanly produced by the $NaBH_3CN$ reduction of cholest-8(14)-en-7-one tosylhydrazone (**1**), and preliminary investigations in our hands



1

2a, $R_1 = D$; $R_2 = H$
b, $R_1 = R_2 = H$
c, $R_1 = H$; $R_2 = D$
d, $R_1 = R_2 = D$