123. Isolation and Characterization of σ-Adducts upon Attempted Vicarious Nucleophilic Substitution with Cationic Arene-Iron Complexes

by **Paul Müller***, **Gérald Bernardinelli**, and **Shahrokh Motallebi**

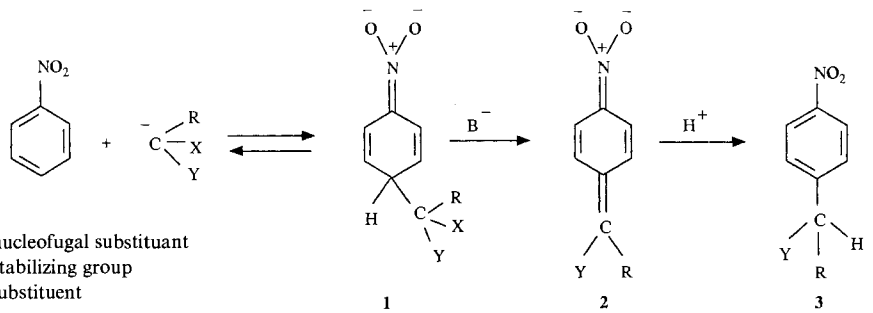
Département de Chimie Organique, Université de Genève, 30, quai Ernest Ansermet, CH-1211 Genève 4

(23.V.90)

Reaction of the carbanions derived from chloromethyl phenyl sulfone or 1-chloroethyl phenyl sulfone with the cationic [Fe(arene)Cp] complexes **8** or **9** produced isolable σ-adducts **10**–**12**. Attempted base induced elimination of the σ-adducts, which would have led to products of vicarious nucleophilic substitution (VNS reaction), failed. Similarly, no VNS products were obtained, when the (arene)tricarbonylchromium complexes **4** were reacted with the anion of chloromethyl phenyl sulfone.

Introduction. – In the vicarious nucleophilic substitution (VNS) reaction [1], an electron-deficient aromatic system such as nitrobenzene reacts with a nucleophile containing a nucleofugal substituent to yield a product corresponding to formal replacement of one of the H-atoms of the aromatic ring by a substituent *(Scheme 1)*. Mechanistically, the reaction proceeds *via* a *Meisenheimer* adduct **1** of the nucleophile to the aromatic, which undergoes base-induced β-elimination to **2**. The substitution product **3** is obtained by protonation of **2**.

Scheme 1



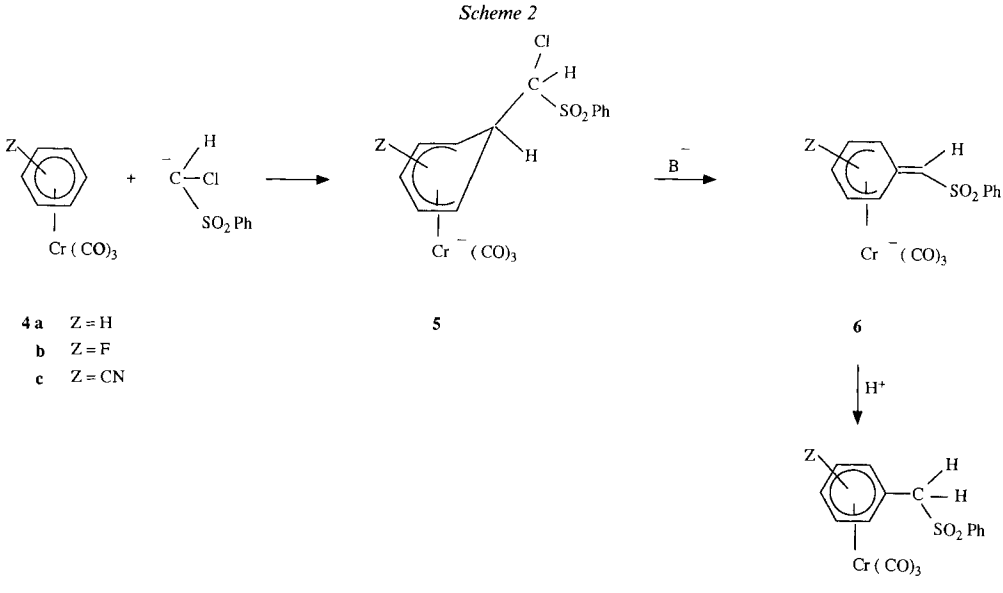
X = nucleofugal substituant
Y = stabilizing group
Z = substituent

Although originally discovered and developed with aromatic nitro compounds, the VNS reaction proceeds with a large variety of other electrophilic aromatics [2]. Among the substituents conveying electrophilic character to the aromatic ring, transition metals can play a prominent role. Indeed, many (η^6-arene)metal complexes exhibit remarkable reactivities towards nucleophilic reagents [3]. It appeared, therefore, possible to realize VNS reactions with compounds, in which the activation is provided by complexation to an appropriate transition metal rather than by an electron-attracting organyl group. This

communication shows that the first step of the sequence, *i.e.* formation of σ-adducts analogous to **1** between complexed aromatics and VNS nucleophiles does indeed occur. However, β-elimination of the adducts resulting in formation of the desired substitution products has, so far, not been realized.

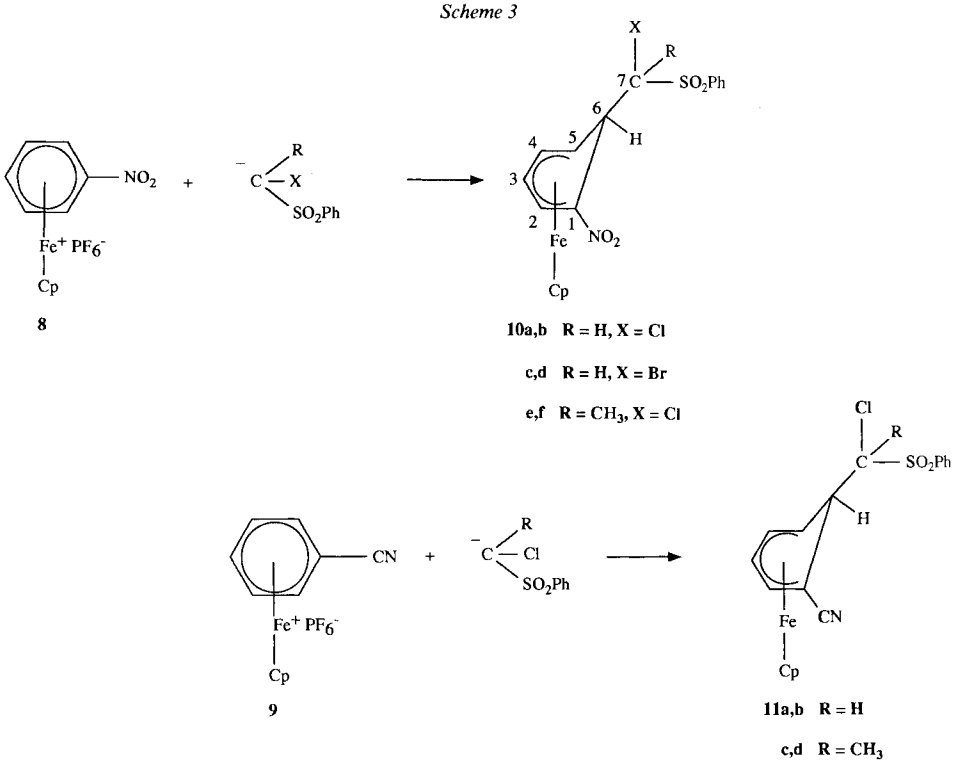
Results and Discussion. Our first experiments were carried out with benzenetricarbonylchromium (**4a**), since it is known that activation of benzene towards nucleophilic substitution by the $Cr(CO)_3$ ligand is of comparable magnitude as that effected by the NO_2 substituent [4] *(Scheme 2)*. However, this system was abandoned, as we found that the anion derived from chloromethyl phenyl sulfone produced no VNS product with this substrate nor with tricarbonyl(fluorobenzene)chromium (**4b**) and tricarbonyl(cyanobenzene)chromium (**4c**). Similar negative results have recently been reported by *Ostrowsky* and *Makosza* [5]. According to [5], the failure of benzenetricarbonylchromium (**4a**) to undergo VNS reactions to **7** should be ascribed to difficulties in the elimination step of the σ-adducts **5**.

Scheme 2



Since σ-adducts of nucleophiles capable of undergoing VNS reactions with benzenetricarbonylchromium have not been directly observed, but only inferred by circumstantial evidence, we investigated reactions with cationic arene Fe(II)Cp complexes [6] which are more reactive towards nucleophiles than their corresponding $Cr(CO)_3$ counterparts, and which form isolable adducts with organolithium compounds [7] and enolates derived from simple ketones [8]. These latter nucleophiles require an additional activating substituent for the reaction to occur. Conceivably, the resulting σ-adducts, which are neutral compounds, should be more prone to base attack than the corresponding anionic adducts of tricarbonylchromium complexes.

Scheme 3



The anion derived from chloromethyl phenyl sulfone reacted under mild conditions with (η^5-cyclopentadienyl)(η^6-nitrobenzene)iron(II) hexafluorophosphate (**8**) [6] or the cyano analogue **9** [6] to yield adducts **10a**, **b** and **11a**, **b**, respectively, as a *ca.* 1:1 mixture of two diastereoisomers, separable by column chromatography *(Scheme 3)*. Similarly, the anion of bromomethyl phenyl sulfone added to **8** to give the stereoisomers **10c** and **10d**. All adducts are semi-crystalline, except **10c**, which afforded suitable crystals for X-ray analysis *(Fig.)*. By coincidence, a chiral crystal was submitted for the structure determination. The absolute configuration of **10c** is (6*R*,7*R*), which corresponds to *threo* at C(6) and C(7). As the structure of **10c** shows, attack of the nucleophile occurs in *exo* mode at C(6) of the arene. *exo*-Configuration at C(6) is also assigned to all other adducts prepared in this study in analogy to that of **10c** and to that of other adducts to Fe(+Cp) complexes of arenes [9]. The ^{1}H-NMR of **10c** can be assigned by comparison with the spectral data *(Table 1)* of the enolate adducts of **8** and **9** available in the literature [6]. The other assignments follow by analogy. In the case of **10a**, for example, H–C(6) appears as a *triplet* at 3.94 ppm, which collapses to a *doublet*, when H–C(7) is replaced by D. Attack at any position other than *ortho* would result in a more complex signal for H–C(6). The same phenomenon occurs with **10b**, where H–C(6) resonates at 3.61 ppm. From the similarity of the spectra, the configuration of **10a** should be *erythro*, and that of **10b** *threo*. This criterion cannot be extended to attribute the configuration of the adducts of **9**, the spectra of the isomers of **11** being too similar.

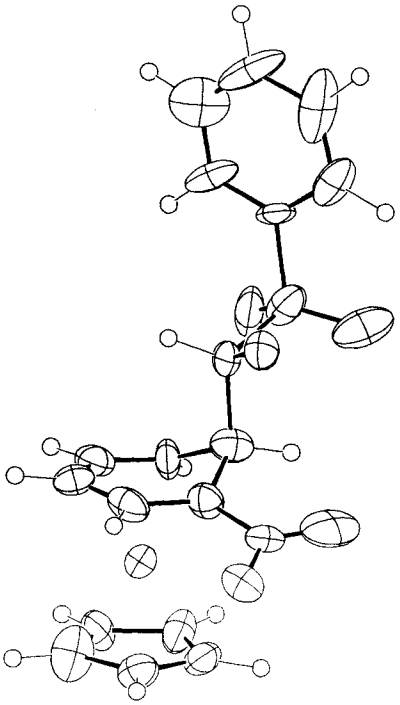


Figure. *X-Ray structure of* **10c**

Table 1. *^{1}H-NMR Data (δ) for Adducts of Cationic Arene-Fe Complexes*

Adduct	Z	R	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Cp	Ar
10a	NO_2	–	5.79	6.19	4.94	4.32	3.94	3.06	4.42	7.45–7.90
10b	NO_2	–	6.00	6.26	4.92	4.48	3.61	3.34	4.43	7.45–7.90
10c	NO_2	–	5.99	6.22	4.89	4.39	3.61	3.35	4.42	7.45–7.90
10d	NO_2	–	5.97	6.15	4.91	4.32	3.99	3.19	4.41	7.50–7.90
10e	NO_2	1.06	6.07	6.15	4.99	3.85	5.00	–	4.40	7.50–8.00
10f	NO_2	1.05	6.03	6.20	5.05	3.83	5.07	–	4.34	7.45–7.90
11a	CN	–	4.97	6.14	4.76	3.48	3.10[a])		4.53	7.50–7.95
11b	CN	–	5.06	6.14	4.70	3.49	3.15[a])		4.53	7.50–7.95
11c	CN	1.23	4.97	6.13	4.74	3.35	3.88	–	4.53	7.45–8.00
11d	CN	1.03	5.06	6.13	4.81	3.50	3.82	–	4.55	7.45–8.00

[a]) Center of *AB* system with H–C(6).

The anion of 1-chloroethyl phenyl sulfone is added in the same fashion to **8** or **9** resulting in *ca.* 1:1 mixtures of semi-solid stereoisomers **10e, f** and **11c, d** respectively, which could be separated by chromatography. In contrast, no adduct was obtained with the carbanion of α-chlorobenzyl phenyl sulfone, and only a 5% yield of adduct **12** resulted with the tris(phenylthio)methane anion.

Reaction of either of the pure diastereoisomers **10a** or **10b** with LDA (1 equiv. at −78° followed by quenching with 10% HCl at 0° produced a *ca.* 1:1 mixture **10a**/**10b**, but no elimination product. Quenching of the reaction mixture from **10a** or **10b** with D_2O resulted in D incorporation at the substituent (C(7)), with loss of the *doublets* at 3.06 (**10a**)

and 3.34 (**10b**), respectively. Similarly, when **10c** was exposed to NaH (20 equiv.) in THF at 25°, a 2:3 mixture **10c**/**10d** resulted. Under reversible conditions (KOH, (D_6)DMSO), **10a** epimerized at C(7), but no H/D exchange occurred at C(6). Analogous results were obtained, when **11a** was exposed to the same reaction conditions. Thus, the predominant isomer of the attachment step to **9** (**11a**), upon treatment with LDA (3 equiv., THF, −78°, 2 h), and quenching, produced a 1:2 mixture **11a**/**11b**. When a mixture **11a**/**11b** was heated with BuLi (−78°, 2 h), the starting compounds were isolated after quenching with H_2O.

With the adducts of 1-chloroethyl phenyl sulfone (**10c**, **d**, and **11c**, **d**), deprotonation at C(7) cannot occur, but they still failed to undergo β-elimination with LDA. At low temperature (−78°), the compounds were recovered unchanged from the reaction mixture, while under more violent conditions (10 equiv. of LDA, −40°, 4 h), total decomposition took place. No isomerization at C(6) resulted, when the pure isomer **11c** was exposed to LDA and recovered under conditions, where the isomers having H-atoms at C(7) epimerize.

Ostrowski and *Makosza* [5] have proposed three reasons, why (arene)tricarbonylchromium complexes do not enter VNS reactions, namely *i*) electrostatic repulsions of the attacking base by the negatively charged CO groups bound to the metal, *ii*) impossibility, for steric reasons, for the σ-adduct **5** to adopt an antiperiplanar conformation of H−C(6) and the leaving group, and *iii*) steric hindrance towards attack of the base by the bulky $Cr(CO)_3$ group.

Since the σ-adducts of Fe^+(Cp) complexes, contrary to those of (arene)tricarbonylchromium are neutral, we do not believe, that electrostatic repulsions of base attack should be an important cause for the lack of reactivity of the former towards elimination. Further, we see no difficulty for the σ-adducts to attain the conformation required for β-eliminations. Although the crystal structure of **10c** *(Fig.)* shows H−C(6) and the bromide in an approximate *gauche*-conformation, which is indeed not favorable for elimination processes, **10c** is not very crowded around C(7), and there is no reason why the antiperiplanar arrangement of H−C(6) and the halide should not be attainable. This hypothesis is corroborated by the observation that equilibration of the pure stereoisomers of **10** in the presence of base leads to *ca.* 1:1 mixtures of stereoisomers. If severe steric hindrance occurred at C(7), one would expect one of the stereoisomers to be formed preferentially. Finally, the question of steric hindrance of the σ-adducts towards base attack should be considered. Conceivably, this might be a problem with sterically strongly crowded bases, such as LDA, but inspection of the X-ray structure of **10c** suggests, that H−C(6) is fairly accessible at least to unhindered bases such as H^- and OH^-.

We believe that the failure of our σ-adducts to undergo elimination is due to a combination of two causes. One of them consists in the low kinetic and thermodynamic acidity of H−C(6). Although proton abstraction with concomitant formation of an anion is not a prerequisite for β-elimination, the elimination does require development of same partial negative charge at C(6). This charge may not be accommodated by the system. The metal is coordinatively saturated and does not accept additional electrons and, further, the additional charge cannot be delocalized into the cyclohexadienyl ligand, since the latter would be an antiaromatic system. The NO_2 (or CN) substituent is locked in the plane of the coordinated centers and cannot provide stabilization, because the H−C(6) bond is situated in a pseudo-equatorial orientation.

The second cause, related to the first one, is provided by the insufficient leaving group abilities of the Cl or Br groups with α-sulfonyl substituents. β-Eliminations with compounds having electron-withdrawing substituents at the β-position usually require rather severe reaction conditions [10], since the developing positive charge is destabilized by the substituent. For such systems, an E_1cB mechanism would be more favorable, but this does not occur for reasons mentioned above.

It is worthwhile to mention that, while generation of a negative charge at C(6) in σ-adducts of (arene)metal complexes does not occur easily, there are numerous examples of generation of (partial) positive charge in this position, as exemplified by the nucleophilic aromatic substitution with complexed aromatic halides [3]. The fact that **10a** gives an 83% yield of α-chloro(*o*-nitro)benzyl phenyl sulfone with DDQ [11] is consistent with these observations, provided it proceeds *via* hydride abstraction at C(6). Unfortunately, the mechanism of these oxidative decomplexation reactions are not well understood, but they probably proceed *via* initial attack on the Cp or cyclohexadienyl ligand, rather than *via* hydride abstraction.

Our observations suggest that elimination with the σ-adducts might be favored by electrophilic catalysis. However, preliminary experiments with *Lewis* acids ($AlCl_3$, $SbCl_5$, $AgBF_4$), which could induce elimination *via* a carbenium ion at C(7), resulted only in decomposition products. This is not too surprising, since such reagents can effect loss of the Cp or cyclohexadienyl ligand [6] in competition with Cl abstraction.

In conclusion, our results show that the VNS reaction does not occur with Fe^+(Cp) complexes of nitrobenzene or benzonitrile under conditions, where the uncomplexed nitrobenzene is reactive, although typical VNS nucleophiles form stable σ-adducts with such complexes. However, we believe still in the possibility of realizing formal VNS reactions with such σ-adducts, by appropriate modifications of the various reaction parameters.

The authors are indebted to the *Swiss National Science Foundation* (project No. 2.602–0.87) for financial support, to Mr. *J. P. Saulnier* for the NMR spectra, and MMe. *O. Vaucher, D. Clément,* and *E. Sandmeyer* for the mass spectra. We also thank *E. P. Kündig* for helpful discussions.

Experimental Part

General. See [12]

Synthesis of (Arene)metal Complexes and Reagents. (η⁶-Benzene)tricarbonylchromium (**4a**) and *tricarbonyl(η⁶-fluorobenzene)chromium* (**4b**) were synthesized according to *Mahaffy* and *Pauson* [13], and *tricarbonyl(η⁶-cyanobenzene)chromium* (**4c**) by exchange of **4b** with CN^- ion [14]. *(η⁵-Cyclopentadienyl)(η⁶-Nitrobenzene)iron hexafluorophosphate* (**8**) and *(η⁶-cyanobenzene)(η⁵-cyclopentadienyl)iron hexafluorophosphate* (**9**) were prepared according to published procedures [6] [15].

Chloromethyl phenyl sulfone and tris(phenylthio)methane were purchased from *Fluka,* while 1-chloroethyl phenyl sulfone and α-chlorobenzyl phenyl sulfone were synthesized according to established methods [16] [17]. Bromomethyl phenyl sulfone was obtained as described by *Makosza* and *Golinski* [18].

Attachment of Anions to (η⁶-Arene)(η⁵-cyclopentadienyl)iron Hexafluorophosphates **8** *and* **9**. *General Procedure.* To a stirred soln. of 1.0 mmol of the appropriate complex **8** or **9** and 1.0 mmol of 1-chloroalkyl phenyl sulfone in dry DMSO (6 ml), 5.0 mmol of powdered KOH were added. An intense color developed immediately, and the soln. was stirred at r.t. for 30 min under N_2. The mixture was then poured into 5% HCl (30 ml) and extracted with $CHCl_3$ (3 × 25 ml). The combined extracts were washed with H_2O (2 × 50 ml). After drying ($MgSO_4$), the solvent was removed on a rotary evaporator and the product isolated by column chromatography. The adducts were obtained as highly colored oils and were reprecipitated from CH_2Cl_2/pentane.

(η⁵-Cyclopentadienyl){1–5-η{6-exo-[chloro(phenylsulfonyl)methyl]-1-nitrocyclohexadienyl}}iron (**10a, b**): 75% yield (1:1 mixture of diastereoisomers) from **8** and chloromethyl phenyl sulfone. The isomers were

separated by column chromatography on silica gel (5 cm) using CH_2Cl_2/toluene 1:1. Anal. calc. for $C_{18}H_{16}ClFeNO_4S$: C 49.83, H 3.69, N 3.23; found: C 49.74, H 3.69, N 3.27.

10a: Semi-crystalline dark-green solid. IR (CH_2Cl_2): 3675*m*, 3053*m*, 2360*m*, 2350*m*, 1610*w*, 1275*w*. ^{1}H-NMR: see *Table 1*. MS: 433 (M^+), 244 (100), 214 (12), 190 (10), 170 (5), 141 (50), 125 (14), 91 (11), 77 (76), 65 (12).

10b: Dark-red semi-crystalline solid. ^{1}H-NMR: see *Table 1*.

(η^5-Cyclopentadienyl){1–5-η-{6-exo-[bromo(phenylsulfonyl)methyl]-1-nitrocyclohexadienyl}}iron (**10c, d**). Obtained in 79% as 0.85:1 mixture of **10c** *(threo)* and **10d** *(erythro)* from **8** and α-bromomethyl phenyl sulfone. Separation by column chromatography (SiO_2, CH_2Cl_2).

10c: Dark-red crystals. M.p. 164 (dec.) (THF). IR (CH_2Cl_2): 3060*w*, 3000*m*, 2300*w*, 1510*m*, 1420*s*, 1320*m*, 1260*s*, 1150*w*, 1080*w*, 840*m*. ^{1}H-NMR: see *Table 1*.

Crystallographic Data of **10c**. Cell parameters and reflection intensities were measured at r.t. on a *Nonius CAD4* diffractometer with graphite monochromated Mo*K*α radiation. A summary of crystal data, intensity measurements and structure refinement is given in *Table 2*. The structure was solved by direct methods (MULTAN-87) and refined by least-square analysis with the X-TAL program [19]. The absolute configuration was confirmed by refinement of the absolute-structure parameter *x* [20].

Table 2. *Crystal Data, Intensity Measurements, and Structure Refinement for* **10c**

Formula	$C_{18}H_{16}NO_4SBrFe$	$(\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.53
Molecular weight	478.1	No. of measured reflections	3730
Crystal system	Orthorhombic	No. of observed reflections	2505
Space group	$P2_12_12_1$	Criterion for observed	$\|Fo\| > 4\sigma(Fo)$
Crystal size [mm]	0.10 × 0.16 × 0.32	No. of parameters	236
a [Å]	9.5411 (12)	Refinement (on *F*)	full-matrix
b [Å]	11.719 (2)	Weighting scheme	$\omega = 1/\sigma^2(F)$
c [Å]	16.072 (2)	H-Atoms	calc.
V [Å^3]	1797.0 (4)	Max. and average Δ/σ	0.275, 0.022
Z	4	Max. and min. $\Delta\rho$ [e·Å^{-3}]	1.23, −1.22
D_c [g·cm^{-3}]	1.77	*S*	2.25
F_{000}	960	Absolute structure parameter *x* [20]	0.05 (2)
μ [mm^{-1}]	3.175	*R*, *wR* [%]	7.1, 5.0

10d: Dark-green, semi-crystalline solid. IR (CH_2Cl_2): 3060*w*, 3000*w*, 2300*w*, 1510*s*, 1310*s*, 1160*m*, 1080*m*, 840*m*. ^{1}H-NMR: see *Table 1*.

(η^5-Cyclopentadienyl){1–5-η-{6-exo-[1-chloro-1-(phenylsulfonyl)ethyl]-1-nitrocyclohexadienyl}}iron (**10e, f**): 65% yield (1:1 mixture of diastereoisomers) from **8** and α-chloroethyl phenyl sulfone. Separation by column chromatography (silica gel, AcOEt/hexane 1:1). IR (CH_2Cl_2): 3675*w*, 3060*w*, 2950*w*, 2360*w*, 2350*w*, 1610*w*, 1510*w*, 1310*m*, 1150*s*, 1010*s*, 810*s*. MS: 244 (100), 214 (21), 198 (6), 186 (12), 160 (4), 150 (8), 137 (26), 121 (26), 103 (18), 91 (22), 77 (69), 65 (22), 51 (22). Anal. calc. for $C_{19}H_{18}ClFeNO_4S$: C 50.95, H 4.02, N 3.13; found: C 51.19, H 4.00, N 2.98.

10e: Green semi-crystalline solid.

10f: Dark-red semi-crystalline solid. ^{1}H-NMR: see *Table 1*.

(η^5-Cyclopentadienyl){{1–5-η-{6-exo-[chloro(phenylsulfonyl)methyl]-1-cyanocyclohexadienyl}}iron (**11a, b**): Obtained in 60% yield (1:2 mixture of diastereoisomers) as orange solids from **9** and α-chloromethyl phenyl sulfone. Separation by column chromatography (aluminum oxide, CH_2Cl_2).

11a: IR (CH_2Cl_2): 3675*w*, 3050*w*, 3000*w*, 2360*m*, 2350*m*, 1619*w*, 1275*w*, 1260*w*, 1150*w*, 1075*w*. ^{1}H-NMR: see *Table 1*. MS: 377 (5), 347 (8), 283 (12), 244 (100), 141 (18), 121 (36), 103 (25), 89 (6), 77 (22), 65 (8), 56 (10). Anal. calc. for $C_{19}H_{19}ClFeNO_2S$: C 55.21, H 3.87, N 3.39; found: C 55.99, H 3.97, N 3.50.

11b: ^{1}H-NMR: see *Table 1*.

(η^5-Cyclopentadienyl){1–5-η-{6-exo-[1-chloro-1-(phenylsulfonyl)ethyl]-1-cyanocyclohexadienyl}}iron (**11c, d**): 55% yield of orange-red solid (1.1:1 mixture of diastereoisomers) from **9** and α-chloroethyl phenyl sulfone. Separation by column chromatography (aluminum oxide, CH_2Cl_2).

11c: IR (CH_2Cl_2): 3675*w*, 3050*w*, 2950*w*, 2350*m*, 2340*m*, 2200*m*, 1675*w*, 1440*w*, 1300*m*, 1150*m*, 106*s*, 1000*s*, 800*s*. ^{1}H-NMR: see *Table 1*. MS: 224 (42), 207 (2), 186 (2), 143 (33), 130 (9), 125 (15), 121 (25), 103 (60), 94 (16), 77 (100), 65 (32), 51 (53). Anal. calc. for $C_{20}H_{19}ClFeNO_2S$: C 56.16, H 4.24, N 3.28; found: C 55.97, H 4.41 N 3.29.

11d: ^{1}H-NMR: see *Table 1*.

(η^5-Cyclopentadienyl){1–5-η-{6-exo-[tris(phenylthio)methyl]-1-nitrocyclohexadienyl}}iron (**12**). Tris(phenylthio)methane (1.0 mmol) and **8** was stirred with 10.0 mmol of powdered KOH in dry DMSO (6 ml) at r.t. for 6 h. The mixture was poured into 5% HCl (30 ml) and extracted with CH_2Cl_2. A dark-red solid was obtained in 5% yield after by column chromatography (silica gel, CH_2Cl_2). IR (CH_2Cl_2): 3675*w*, 3065*w*, 3000*w*, 2300*w*, 1720*w*, 1620*w*, 1510*w*, 1475*w*, 1450*w*, 1320*m*, 900*m*, 725*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.35–7.80 (*m*, 5 H); 6.50 (*t*, 1 H); 5.89 (*d*, 1 H); 4.91 (*t*, 1 H); 4.55 (*d*, 1 H); 4.21 (*s*, 5 H); 3.40 (*t*, 1 H). MS: 460 (*s*), 339 (34), 307 (18), 161 (10), 231 (15), 218 (100), 199 (10), 186 (16), 154 (14), 135 (10), 121 (19), 109 (100), 94 (15), 77 (28), 65 (41), 51 (23).

Reaction of (η^6-Arene)tricarbonylchromium Complexes **4** *with Chloromethyl Phenyl Sulfone.* Lithium diisopropylamine (1.0 mmol) was prepared from (i-Pr)$_2$NH (1.0 mmol) and BuLi (0.63 ml, 1.6M in hexane) at 0° in 5.0 ml of THF. After stirring the soln. for 20 min, chloromethyl phenyl sulfone (190 mg, 1.0 mmol) was added rapidly. The color changed immediately to yellow. After 1 h at 0°, a soln. of *(η^6-arene)tricarbonylchromium* **4** (1.0 mmol in THF) was added, and the mixture was stirred for 12 h at 50°. After workup of the mixture, TLC and NMR showed that no reaction had occurred.

Attempted Elimination with σ-Complexes **10** *and* **11**. To a stirred soln. of σ-adduct (0.04 mmol) in THF (5 ml) at –78°, LDA (0.05 mmol) in dry THF (5 ml was added). The resulting mixture was stirred at –78° for 1 h, after which it was quenched with 10% HCl (10 ml) at –78°. After warming up to r.t., the reaction flask was washed with CH_2Cl_2 (10 ml). The solvents were evaporated *in vacuo*, and the residue was treated with aq. NH_4PF_6 (20 ml, 0.05 mmol) in the hope of precipitating cationic complexes by protonation of intermediates analogous to **6**. The mixture was extracted with $CHCl_3$ (3 × 25 ml), the combined extracts were washed with H_2O and dried ($MgSO_4$). After evaporation of the solvent, the product was analyzed by ^{1}H-NMR.

REFERENCES

[1] M. Makosza, J. Winiarski, *Acc. Chem. Res.* **1987,** *20,* 282; K. Wojciechowski, M. Makosza, *Synthesis* **1989,** 106; M. Makosza, Z. Owczarcyk, *J. Org. Chem.* **1989,** *54,* 5094.

[2] M. Makosza, J. Golinski, A. Rykowski, *Tetrahedron Lett.* **1983,** *24,* 3277; S. Ostrowski, M. Makosza, *Tetrahedron* **1988,** *44,* 1731; M. Makosza, T. Glinka, S. Ostrowaki, A. Rykowski, *Chem. Lett.* **1987,** 61; R. A. Murphy, Jr., M. P. Cava, *Tetrahedron Lett.* **1984,** *25,* 803.

[3] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, California, 1987.

[4] M. F. Semmelhack, *Ann. N. Y. Acad. Sci.* **1982,** *1,* 1053; M. F. Semmelhack, G. R. Clark, J. L. Garcia, J. J. Harrison, Y. Thebtaranoth, W. A. Wulff, A. Yamashita, *Tetrahedron* **1981,** *37,* 3957.

[5] S. Ostrowski, M. Makosza, *J. Organomet. Chem.* **1989,** *367,* 95.

[6] C. C. Lee, U. S. Gill, M. Iqbal, C. I. Azogu, R. G. Sutherland, *J. Organomet. Chem.* **1982,** *231,* 151.

[7] D. Astruc, *Tetrahedron* **1983,** *39,* 4027.

[8] R. G. Sutherland, R. L. Chowdhury, A. Piorko, C. C. Lee, *Can. J. Chem.* **1986,** *64,* 2031.

[9] I. U. Khand, P. L. Pauson, W. E. Watts, *J. Chem. Soc. (C)* **1969,** 2024; S. G. Davies, M. L. H. Green, D. M. P. Mingos, *Tetrahedron* **1978,** *34,* 3047; P. L. Pauson, *J. Organomet. Chem.* **1981,** *200,* 207; J. C. Boutonnet, E. Rose, *ibid.* **1981,** *221,* 157; C. C. Lee, U. S. Gill, R. G. Sutherland, *ibid.* **1984,** *267,* 167.

[10] R. P. Holysz, *J. Am. Chem. Soc.* **1953,** *75,* 4432.

[11] R. G. Sutherland, R. L. Chowdhury, A. Piorko, *J. Org. Chem.* **1987,** *52,* 4618.

[12] P. Müller, J.-P. Schaller, *Helv. Chim. Acta* **1989,** *72,* 1608.

[13] C. A. L. Mahaffy, P. L. Pauson, *Inorg. Synth.* **1979,** *19,* 154.

[14] M. F. Semmelhack, *J. Organomet. Chem.* **1976,** *361,* 1.

[15] E. I. Sirotkina, A. N. Nesmeyanov, N. A. Vol'kenau, *Dokl. Akad. Nauk, SSSR, Ser. Khim.* **1969,** 1524.

[16] M. Makosza, T. Glinka, A. Kinowski, *Tetrahedron* **1984,** *40,* 1.

[17] B. B. Jarvis, J. C. Sankaitis, *J. Am. Chem. Soc.* **1973,** *95,* 7708.

[18] M. Makosza, J. Golinski, *J. Org. Chem.* **1984,** *49,* 1488.

[19] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq, M. M. Woolfson. 'A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data', Universities of York, England, and Louvain-la Neuve, Belgium, 1980; 'XTAL2.4. Users Manual', Eds. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1988.

[20] G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985,** *41,* 500.