SYNTHESIS AND CONFORMATIONS OF CHROMIUM TRICARBONYL SUBSTITUTED DIARENES

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Summary

The metallation of a series of seven planar and bent diarenes has been examined to determine the conformations of the mono- and dimetallated products. It has been found that bent diarenes can be metallated on either the convex (*syn*) or concave (*anti*) faces of the arene. In the absence of other directing groups, metallation at the concave face is favored. Dimetallation of planar diarenes results in exclusive *trans* metallation. Dimetallation of bent diarenes yields the *trans* isomer as the major species, but *cis* dimetallation of the convex face is also observed. Conformational assignments have been made using ^{1}H and ^{13}C NMR spectral evidence.

Introduction

The direct reaction of arenes with chromium hexacarbonyl to prepare arene chromium tricarbonyl complexes is usually complicated by the high vapor pressure of the metal carbonyl which results in the persistent sublimation of the metal carbonyl from the reaction mixtures. This problem is exacerbated by the fact that the reactions between arenes and chromium hexacarbonyl are generally slow even in refluxing butyl ether or dimethoxyethane. A variety of techniques have been developed to overcome the problem of sublimation including the use of sealed tube reactions [1] and the use of a complex, self-rinsing reflux head designed by Strohmeier [2].

Two recent reviews have described the synthesis of arene chromium tricarbonyl complexes [3,4]. Several workers have avoided the problems associated with chromium hexacarbonyl by using highly reactive intermediates such as triammine-chromium tricarbonyl [5] or tris(acetonitrile)chromiumtricarbonyl [6] in reactions with arenes using refluxing THF or dioxane as the solvent. These intermediates give good yields, but the time necessary to prepare the intermediates detracts from their usefulness.

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The recent development of a mixed solvent system (90% butyl ether: 10% THF) for the direct reaction of arenes with chromium hexacarbonyl has made it possible to prepare a wide variety of arene chromium tricarbonyl complexes in good yields [7,8]. This method is particularly effective for the synthesis of dimetallated species which are produced in poor yields (if at all) by other direct and indirect methods.

We have recently reported the synthesis of a series of biphenyl bis(chromium dicarbonyl)-μ-diphosphine and diarsine complexes [9]. These complexes are prepared from biphenyl bis(chromium tricarbonyl) which is produced in excellent yield by the method of Top and Jaouen [7]. As a test of the versatility of the Top and Jaouen procedure we have used this method to prepare a series of singly and doubly metallated diarenes. In this paper we shall describe the results of these syntheses and discuss the conformations of the resulting compounds.

Results

The reaction of compounds I–VII, Table 1, with chromium hexacarbonyl in 9/1 butyl ether/THF have been conducted. In most cases a 2/1 molar ratio of metal carbonyl to diarene was used to drive the reactions toward dimetallation. During the reactions, which typically require three to five days, dimetallated products are found to precipitate from solution along with small quantities of a blue-green chromium-containing decomposition product.

Using the procedure of Top and Jaouen we have prepared mono- and dimetallated compounds whose melting point and analytical data are listed in Table 1. Infrared carbonyl stretching frequencies and the ^{1}H NMR spectra are presented in Table 2, while ^{13}C NMR spectral data of selected compounds are presented in Table 3.

Reaction of I, II, and III with chromium hexacarbonyl produce reaction mixtures which were shown by HPLC to contain two reaction products. In each case, hot heptane extraction of the mixture removed one of the two components which could be shown by ^{1}H NMR to be the mono-metallated product, Ia, IIa or IIIa. The residue from heptane extraction was recrystallized from benzene/pentane to give bimetallated products, Ib, IIb or IIIb. ^{1}H NMR of compounds Ib and IIIb contain sharp singlets for the methylene protons requiring that these compounds be *trans* dimetallated. The ethylene resonance in the spectrum of IIb gives a clear AA'BB' pattern, and, by analogy, we have assigned this compound a *trans* geometry.
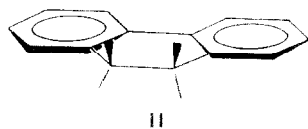

I

II

TABLE 1

ANALYTICAL DATA AND MELTING POINTS FOR DIARENE CHROMIUM TRICARBONYL
COMPOUNDS

Compound		M.p. (°C)	Analysis (Found (calc) (%))	
			C	H
I Fluorene				
Ia	mono	123–124 (lit. 138–139 [28])		
Ib	di-*trans*	210 (dec.)	51.61 (52.05)	2.23 (2.28)
II 9,10-Dihydrophenanthrene				
IIa	mono	102–104	64.01 (64.56)	3.82 (3.80)
IIb	di-*trans*	169 d	53.38 (53.10)	2.68 (2.65)
III 9,10-Dihydroanthracene				
IIIa	mono	140–141 (lit. 143–145 [29,30])		
IIIb	di-*trans*	182 d (lit. 242 [12a])	53.17 (53.10)	2.90 (2.65)
IV cis-9,10-Dihydro-9,10-dimethylanthracene				
IVa	mono-*anti*	179–181	65.98 (66.28)	4.60 (4.65)
IVb	di-*trans*	201–203 (dec.)	55.18 (55.00)	3.47 (3.33)
V 9,10-Ethenoanthracene				
Va	mono-*syn*	164–165 (dec.)	66.80 (67.06)	3.72 (3.53)
Vb	mono-*anti*	159–160 (dec.)	67.36 (67.06)	3.63 (3.53)
Vc	di-*trans*	234–235 (dec.)	56.07 (55.46)	2.64 (2.52)
VI 9,10-Ethanoanthracene				
VIa	mono-*syn*	189–190 (186 (dec.) [5b])	66.38 (66.67)	4.22 (4.09)
VIb	mono-*anti*	168 (dec.)	66.59 (66.67)	4.27 (4.09)
VIc	di-*trans*	199–203 (dec.)	54.99 (55.23)	2.87 (2.93)
VII 1,2,4,5-Dibenzocycloheptane				
VIIa	mono	122–124	65.26 (65.45)	4.09 (4.24)
VIIb	di-*trans*	197–199	54.39 (54.08)	3.07 (3.00)
VIIc	di-*cis*	169–173	53.63 (54.08)	3.07 (3.00)

Metallation of IV gave a complex reaction mixture which was shown by HPLC to contain one major, insoluble component, IVa, and at least three other minor components. Partial purification of the minor components was achieved by medium pressure column chromatography on silica gel, but attempts to further purify the

TABLE 2

INFRARED AND ^{1}H NMR SPECTRAL DATA FOR DIARENE CHROMIUM TRICARBONYL COMPOUNDS

| Compound	IR (cm^{-1}) [a]	^{1}H NMR chemical shifts (δ (ppm))
Ia	1965, 1888	7.25 (m, 4H), 6.00 (m, 1H), 5.82 (m, 1H), 5.34 (m, 2H), 3.94 (s, 2H) [b]
Ib	1967, 1895	4.80 (m, 2H), 4.56 (m, 2H), 4.35 (m, 4H), 3.10 (s, 2H) [c]
IIa	1965, 1889	7.53 (m, 1H), 7.23 (m, 3H), 5.60 (m, 1H), 5.38 (m, 3H), 2.99–2.58 (m, 4H) [b]
IIb	1960, 1897	4.71–4.28 (m, 8H), 2.70–1.59 (AA'BB', 4H) [c]
IIIa	1968, 1898	7.23 (s, 4H), 5.34 (AA'BB', 4H), 4.06–3.47 (AB, 4H) [c]
IIIb	1967, 1894	4.42 (AA'BB', 8H), 2.78 (s, 4H) [c]
IVa	1967, 1888	7.23 (s, 4H), 5.34 (s, 4H), 3.75 (q, J 7.4 Hz, 2H), 1.55 (d, J 7.4 Hz, 6H) [b]
IVb	1961, 1882	4.81–4.33 (m, 8H), 2.84 (q, J 6.9 Hz, 2H), 1.08 (d, J 6.9 Hz, 6H) [c]
Va	1960, 1880	7.24 (m, 2H), 7.02 (m, 4H), 5.36 (AA'BB', 4H), 4.82 (t, J 3.0 Hz, 2H) [c]
Vb	1961, 1884	7.28–6.87 (m, 6H), 5.64 (m, 2H), 5.05 (m, 2H), 4.91 (m, 2H) [c]
Vc	1971, 1890	6.36 (m, 2H), 5.15 (m, 2H), 4.53 (m, 4H), 4.13 (m, 2H), 3.49 (m, 2H) [c]
VIa	1960, 1876	7.18 (m, 4H), 5.32 (AA'BB', 4H), 4.03 (m, 2H), 2.19–1.65 (AA'BB', 4H) [b]
VIb	1964, 1882	7.23 (m, 4H), 5.33 (AA'BB', 4H), 4.03 (s, 2H), 1.72 (s, 4H) [c]
VIc	1964, 1890	4.90 (m, 2H), 4.54 (m, 4H), 4.25 (m, 2H), 2.68 (s, 2H), 1.93–0.84 (AA'BB', 4H) [c]
VIIa	1968, 1890	7.15 (s, 4H), 5.20 (m, 4H), 4.33 (AB, 2H), 3.15 (m, 4H) [b]
VIIb	1968, 1890	5.51 (AA'BB', 8H), 3.65 (s, 2H), 2.97 (AA'BB', 4H) [c]
VIIc	1970, 1888	4.31 (s, 8H), 4.06 (d, J 15.5 Hz, 1H), 1.95 (d, J 15.5 Hz), 2.60–1.73 (AA'MM', 4H) [c]

[a] IR spectra in CHCl$_3$. [b] CDCl$_3$ solvent. [c] C$_6$D$_6$ solvent.

VII

III R=H
IV R=CH$_3$

VI

V
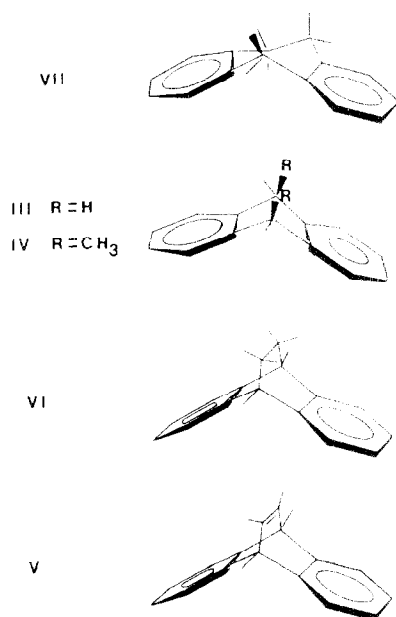
TABLE 3

^{13}C NMR PARAMETERS FOR DIARENE CHROMIUM TRICARBONYL COMPOUNDS (δ (ppm))

| Compound	Carbonyls	Unmetallated rings	Metallated rings	Substituents	Solvent
II		137.35 134.53 128.10 127.35 126.94 123.69		29.08	
IIa	233.25	136.96 130.42 129.16 128.56 127.10 123.09	109.09 104.10 93.95 92.14 91.08 87.00	28.68 27.85	CDCl$_3$
IIb	233.42		110.63 107.70 93.46 91.49 (2C) 85.74	27.18	C$_6$D$_6$
III		136.66 127.39 126.07		36.13	CDCl$_3$
IIIa	232.38	133.34 127.44 126.85	107.85 92.62 91.30	34.37	CDCl$_3$
IV		140.56 127.82 126.24		40.11 28.40	CDCl$_3$
IVa	232.85	137.75 127.79 126.98	111.84 92.28 91.67	39.52 28.66	CDCl$_3$
IVa	233.19	137.80 127.19 third resonance obscured by solvent	111.56 92.08 91.44	39.49 28.50	C$_6$D$_6$
IVb	233.30 232.84		112.67 110.78 91.48 90.70 (2 C) 90.34	35.83 16.50	C$_6$D$_6$
V		139.39 124.39 123.00		146.12 (ethylene) 51.25	CDCl$_3$
Vc	233.48 233.40		118.89 (2C) 94.10 93.20 91.56 (2C)	139.65 45.20	(CD$_3$)$_2$SO
VI		143.91 125.57 123.28		44.22 26.77	
VIc	234.00 231.59		117.69 111.51 91.15 90.79 90.62 90.17	39.99 29.09	C$_6$D$_6$
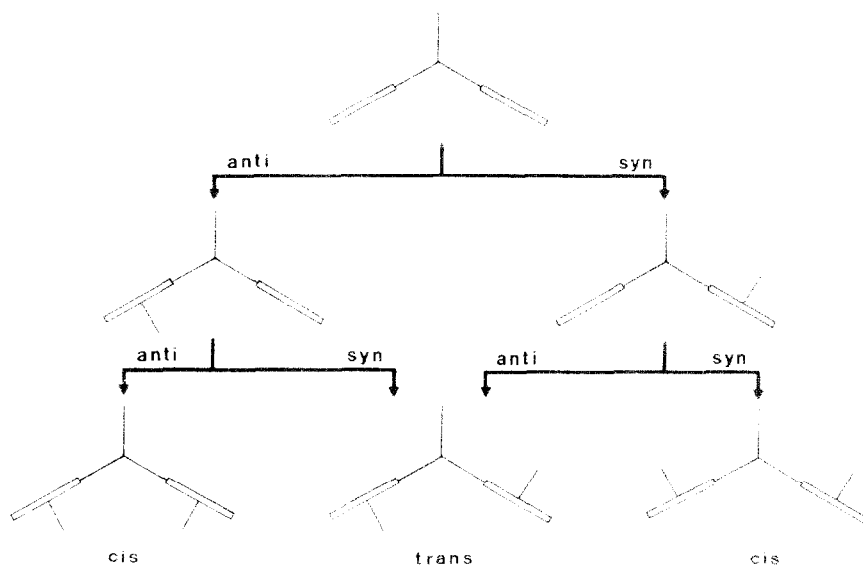
Fig. 1. Substitution patterns for metallation of bent diarene compounds.

minor components using thick layer chromatography resulted in the decomposition of the compounds. The major reaction product, IVa, which was purified by recrystallization from benzene/pentane, was shown by ^{1}H NMR to be a singly metallated compound. Reaction of this compound with triamminechromium tricarbonyl in refluxing dioxane gave one product which was shown by HPLC to be identical to one of the three unrecovered minor products of the original reaction. ^{1}H NMR established that this compound, IVb, was dimetallated.

The conformations of compounds IVa and IVb have been determined by ^{13}C NMR. In principle, two mono-metallated and three dimetallated isomers of a bent diarene can be produced although the cis (anti, anti) isomer should be forbidden on steric grounds. These isomers are illustrated in Fig. 1. Both cis dimetallated isomers are expected to have a singlet carbonyl resonance in the ^{13}C NMR spectrum and three ring carbon resonances. The trans isomer is expected to have two carbonyl resonances and six ring carbon resonances. The ^{13}C NMR spectrum of IVb was found to have two carbonyl resonances and five ring carbon resonances. The observed pattern is only consistent with a trans geometry. It is believed that two of the ring carbon resonances are accidentally superimposed at the resolution of the NMR instrument.

As shown in Fig. 1, metallation of a bent diarene can yield two mono-metallated isomers in which the chromium moieties are syn or anti relative to the alkyl groups on the diarene. As will be discussed below, metallation of the syn isomer is expected to give rise to both the cis(syn, syn) and trans isomers, while the anti isomer would produce the trans isomer and the sterically unfavorable cis (anti, anti) isomer. Since only the trans isomer is observed in the metallation of IVa, it is likely that IVa is the anti isomer.

Further support for the assignment of IVa to the anti isomer comes from the

relative chemical shifts of the methyl carbons in IV, IVa and IVb. The chemical shifts of these carbons are found to be 28.85, 28.50 and 16.50 ppm, respectively. Introduction of the first chromium tricarbonyl moiety has little effect on the chemical shift of the methyl group, whereas the second chromium tricarbonyl exerts a strong upfield shift to the methyl resonance. This effect can be explained if the first metallation occurs *anti* to the methyl groups while the second metallation is *syn* to the methyls. The anisotropy of the chromium tricarbonyl moiety would be expected to have the greatest effect on the chemical shift of the methyl groups when it is immediately adjacent to them.

The metallation of V with triamminechromium tricarbonyl in refluxing dioxane has been reported by two groups [5b,10]. Trahanovsky and Baumann [10] reported the isolation of a mono-metallated isomer from this reaction. Subsequent reduction of this compound to the mono-metallated VI derivative was accomplished by hydrogenation over Pd(C) in dioxane. ^{1}H NMR of the mono-metallated derivative of VI showed that the ethano bridge proton resonance was split into an AA'BB' pattern which was attributed to *syn* metallation. By inference, the mono-metallated derivative of V was assumed to be the *syn* derivative.

Moser and Rausch [5b] have reported the isolation of a mono-metallated isomer of V which appears to be identical to that reported by Trahanovsky and Baumann. In addition, Moser and Rausch isolated a small amount of a second product which analyzed for a dimetallated product. It was assumed to be the *cis(syn, syn)* derivative on the basis of steric arguments.

In our research, reactions of compounds V and VI with chromium hexacarbonyl gave reaction mixtures which were shown by HPLC to contain four reaction products. For each reaction, the third component, Vc or VIc, was found to be the major product. Extraction of the reaction mixtures with hot heptane removed the minor components which were separated by medium pressure column chromatography on silica gel. In both cases, the fourth components, Vd and VId, decomposed during workup. The major components, Vc and VIc, could be recrystallized from methylene chloride/pentane.

^{1}H NMR spectra of compounds Va and Vb shown them to be mono-metallated isomers. The spectrum of Va is found to be identical to that reported by Trahanovsky and Baumann for the *syn* isomer. We infer that Vb is the *anti* isomer. Likewise, ^{1}H NMR spectra of compounds VIa and VIb show that these compounds are mono-metallated and VIa was found to be identical to the *syn* isomer previously reported. It should be noted that the ethano bridge proton resonance in compound VIb is found to be a broad singlet which supports the assignment of the *anti* geometry to this compound.

^{1}H NMR of compounds Vc and VIc indicate that these compounds are dimetallated. The complexity of the ring proton resonances for both compounds and the well defined AA'BB' multiplet of the ethano bridge resonance of VIc indicate that both compounds are probably *trans* dimetallated. The *trans* geometry of compounds Vc and VIc has been confirmed by ^{13}C NMR.

If we assume that the fourth reaction product which decomposed upon workup is the *cis (syn, syn)* isomer, then the reaction mixtures of both V and VI elute in the order *syn, anti, trans, cis*. Relative areas of the HPLC peaks indicate that *syn* metallation is favored over *anti* metallation for compound V, while the reverse is true for compound VI. The *cis* isomer contributes a minor component from both

reactions, but it is relatively more abundant in the reaction of V than it is in the reaction of VI. A possible explanation for these preferences is discussed below.

Metallation of VII produced three reaction products which could be separated by a two step extraction. Compound VIIa was found by ^{1}H NMR to be the mono-metallated product while VIIb and VIIc were found to be the *trans* and *cis* dimetallated isomers, respectively. HPLC of the reaction mixture showed that the compounds eluted in the order mono, *trans*, *cis* as did the metallation products of V and VI.

Discussion

As noted in the Introduction, relatively few examples of bis(chromium tri-carbonyl) substituted diarenes have been reported. Rausch and his coworkers [5] have reported the synthesis of dimetallated biphenylene and Luzikov, et al. [11] have prepared *trans*-bis(chromium tricarbonyl)-3-methylfluorene. Rausch has reported the synthesis of trace amounts of bimetallated V, and Reinke and Oehme have reported the synthesis of *trans*-bis(chromium tricarbonyl)-9,10-dihydroanthracene [12]. Recently, Afanasova, et al. [13] have reported that tetramethyl-9,10-dis-ilaanthracene (VIII) can be metallated by chromium hexacarbonyl in refluxing butyl ether to give three products which were shown by ^{1}H NMR and X-ray crystallogra-phy to be the mono-metallated, *trans* and *cis* dimetallated products. The relative ease in obtaining this last set of compounds is probably related to the electron-donating ability of the dimethylsilicon groups which activate the rings to metalla-tion.

The metallation of arenes with ferrocene in the presence of aluminum chloride to generate arene iron cyclopentadienyl cations has been studied extensively [14] and two groups have examined the mono- and dimetallated products which arise from metallation of diarenes. For example, the reaction of I and III with ferrocene was reported to give mono-metallated and *trans* dimetallated products [15,16]. Hendrickson and his coworkers reported that metallation of VII with ferrocene gave a mono-metallated product and a mixture of *trans* and *cis* dimetallated products. The dimetallated products could be separated by thin layer chromatography, but bulk separation was not possible. Reaction of ferrocene with IV is reported to give *syn* and *anti* mono-metallated products in a 40/60 ratio as well as the *trans* isomer [17]. Sutherland and his coworkers [18] have recently reported the metallation of the heterocyclic compounds IX–XIII. Compounds IX, XII and XIII are metallated with ferrocene to give mono- and *trans* dimetallated products, while compounds X and XI also gave *cis* isomers.
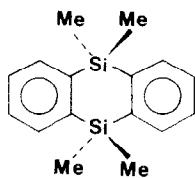
VIII
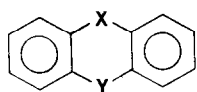
	X	Y
IX	O	O
X	S	O
XI	S	S
XII	NH	O
XIII	NH	S

Sutherland has proposed that mono-metallation of planar diarenes such as IX and XII, and by extension I and II, gives rise to a species illustrated in Fig. 2a which, because of the steric bulk of the organometallic moiety, favors *trans* dimetallation. In contrast, diarenes which exist in a bent or folded geometry such as X and XI are metallated to give a pair of isomers shown in Figs. 2b and 2c. Dimetallation of the isomer shown in Fig. 2b in which the metal moiety is on the concave face of the bent diarene should give rise to exclusive *trans* dimetallation, while metallation of the isomer shown in Fig. 2c, where the metal is on the convex face, can give rise to either *trans* or *cis* dimetallation. For bent compounds such as III, X and XI, the two monometallated isomers might be in equilibrium, but not for rigid, bent compounds such as IV, V and VI.

The arguments presented by Sutherland, et al. [18], to explain the geometries of bis(iron cyclopentadienyl)diarenes dications are entirely applicable to the chromium tricarbonyl derivatives. The planar diarenes I and II give exclusive *trans* bimetallation while the bent diarenes IV–VIII give mixtures of products from which the *cis* compounds can occasionally be isolated. Compound III is known to be bent with a dihedral angle of 148° [19], but only the *trans* dimetallated product has been isolated or observed. It is possible that the arene rings in III can freely fold about the coupling methylene groups giving the concave (*anti*) monometallated isomer as
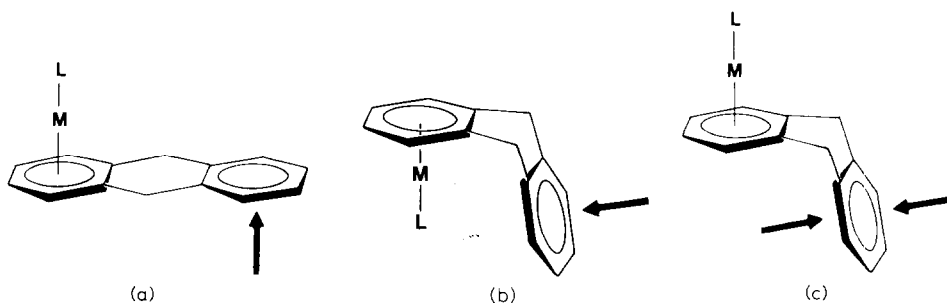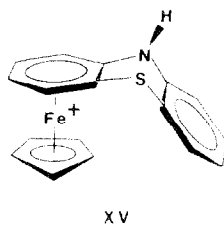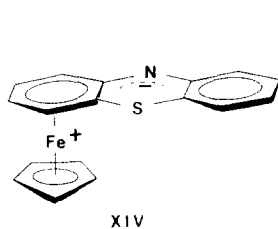

Fig. 2. Metallation pathways for monosubstituted diarene compounds. (a) *Trans* metallation of monosubstituted planar diarenes. (b) *Trans* substitution of *anti* monosubstituted diarenes. (c) *Cis* and *trans* metallation of *syn* monosubstituted diarenes.

XIV

XV

the lowest energy conformation. [*Note*: Sutherland, et al. [18], have observed that although XIII should have a bent configuration it does not give rise to a *cis* dimetallated product. They suggest that the mono-metallated derivative XIII may lose the nitrogen-bound proton to generate a zwitterionic species, XIV, in which the arene moiety is planar. Alternatively, we suggest that the nitrogen-bound hydrogen may favor a position *exo* to the metal which would serve to force the molecule into the conformation shown in XV.] Metallation of this isomer results in the formation of the *trans* product as the exclusive dimetallated species.

The present study has presented an opportunity to examine the structural and electronic factors which control the orientation of metallation in diarenes. Metallation of IV by chromium hexacarbonyl should produce both a *syn* and *anti* metallated product, but only the latter is isolated from the reaction mixture. The *syn* compound is either formed in small amounts or is unstable under the reaction conditions. Compounds V and VI are metallated to yield both the *syn* and *anti* products, but compound V with its exocyclic double bond favors *syn* metallation

XVI

XVII

XVIII

XIX
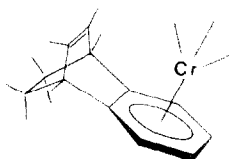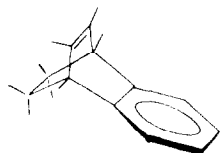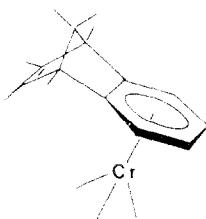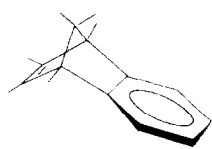
while VI favors *anti* attack. As the geometries of V and VI should be very similar, it would appear that the exocyclic double bond of V acts to bind a chromium carbonyl moiety in an intermediate complex from which it can then attack the *syn* face of the diarene. In the absence of the double bond, the *anti* face is the perferred site of attack.

The directing effect of exocyclic double bonds has been observed by several workers [20–23]. Compound XVI has been metallated to give predominantly or exclusively the *syn* (relative to the double bond) product, XVII [20]. Trahanovsky and his coworkers [21] have found that metallation of XVIII gave the *syn* product, XIX, as the exclusive product.

In the absence of a secondary directing effect, metallation of bent diarenes occurs at the concave face of the diarene even though this face should be less sterically favorable. We suggest that metallation of the concave face is favored because of the enhanced electron density which would be found in the region of space between the arene rings.

Experimental

Diarene compounds I, II, III and VII were purchased from Aldrich and used as received. Compounds IV [24], V [25], and VI [26] were prepared by literature procedures. All compounds were examined by ^{1}H NMR and HPLC to establish purity. Chromium hexacarbonyl was purchased from Strem Chemicals. Triamminechromium tricarbonyl was prepared from a procedure developed by McNeese [27]. Butyl ether and THF were dried over CaH_2 and distilled under N_2. All reactions were conducted under N_2.

Medium pressure column chromatography was conducted with an Altex 15 × 500 mm column using a Fluid Metering, Inc. Model RPSY pump. Merck LiChroprep Si60 was used as a solid phase and 10/1 ligroin/THF was used as the eluant. High pressure column chromatography was conducted using a Gow-Mac Model 080-20 HPLC outfitted with a Whatman Partisil PXS 10/25 column. The eluant for HPLC was a 7/3 mixture of ligroin and THF.

NMR spectra were recorded on a Varian FT80A NMR Spectrometer operating at room temperature. IR spectra were recorded on a Perkin–Elmer 467 Grating Spectrometer. Analyses were conducted by Micro Analysis, Inc. of Wilmington, DE.

Synthesis of diarene complexes

Using a procedure adapted from Top and Jaouen [7], a 250 ml round bottom flask outfitted with a spin bar and a reflux condenser was charged with 10 mmol of diarene and 20 mmol of chromium hexacarbonyl. The flask was flushed with N_2 and 130 ml of butyl ether and 15 ml of THF were added. The reaction mixture was refluxed for 4–5 d during which time a yellow precipitate was generally found to form. At the end of the reaction time, the reaction mixture was cooled and filtered affording a solid which contained the dimetallated complex contaminated with a blue chromium-containing decomposition product. This solid was taken up in hot benzene and filtered. Pentane was added to the warm benzene solution and the solution was allowed to cool yielding crystals of the dimetallated complexes in good yield. These compounds can be further purified by recrystallization from either benzene/pentane or methylene chloride/pentane mixtures.

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The reaction mixture filtrate from above was stripped under vacuum to remove butyl ether and THF. Unreacted chromium hexacarbonyl sublimes from the reaction mixture during this process. The yellow solid which remained was extracted with hot heptane leaving small quantities of dimetallated material which could be purified as described above.

In cases where only one mono-metallated product was produced, this compound was recovered in good yields and purity from the cooled heptane extract. In cases where several compounds were present, the mixture was separated by chromatography on a medium pressure silica gel column.

Synthesis of trans-[bis(chromium tricarbonyl)-cis-9,10-dihydro-9,10-dimethylanthracene (IVb)

A 250 ml reaction flask outfitted with a spin bar and a reflux condenser was charged with 1.71 g (5.0 mmol) *anti*-chromium tricarbonyl-*cis*-9,10-dihydro-9,10-dimethylanthracene (IVa) and 3.0 g (15 mmol) triamminechromium tricarbonyl. 100 ml of dry, degassed dioxane was added to the flask and the reaction mixture refluxed overnight. Dioxane was removed from the reaction mixture under vacuum and the resulting yellow solid was extracted four times with 25 ml of hot 9/1 heptane/benzene. The remaining yellow solid was recrystallized from benzene/pentane to give IVb as a yellow solid.

Acknowledgements

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