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Arene tricarbonyl complexes of chromium (0), molybdenum (0), and tungsten (0)

Darrell Keith Wells
Iowa State University

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ARENE TRICARBONYL COMPLEXES OF CHROMIUM(0), MOLYBDENUM(0), AND TUNGSTEN(0)

by

Darrell Keith Wells

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1969

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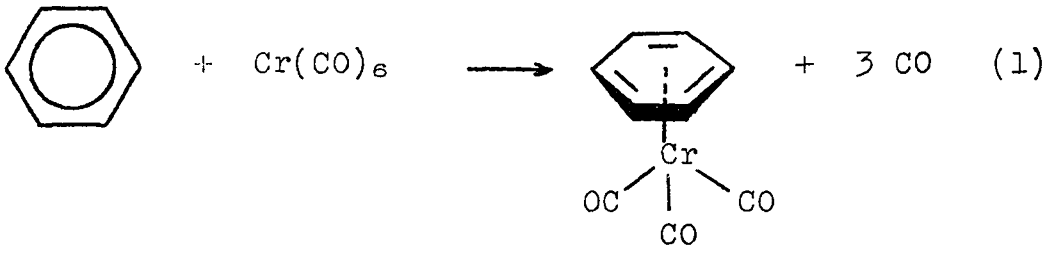
CHAPTER I. HISTORICAL

The first of the (arene)tricarbonylchromium complexes was prepared by Fischer and Öfele in 1957 (1); heating benzene and hexacarbonylchromium together at 200° in a sealed tube gave small yields of the (benzene)tricarbonylchromium, 1, whose structure and bond lengths were determined by Bailey and Dahl (2): Cr-C(ligand CO) distance 1.84 Å; C-O(carbon monoxide), 1.14 Å; Cr-C(ligand benzene), 2.22 Å; C-C(benzene), 1.40 Å; Cr-ring, 1.72 Å; ∠(OC-Cr-CO), 88°; ∠(C-C-C(benzene)), 120°.



1

The valence bond approach predicts that the complexed chromium(0) uses six vacant sp^3d^2 orbitals to accept the twelve electrons from the benzene ring and the three carbon monoxide ligands; the three two-electron centers in the benzene ring and the three carbon monoxides can be thought to occupy the six corners of an octahedron. The six electrons in the uncomplexed chromium(0) atom, in the

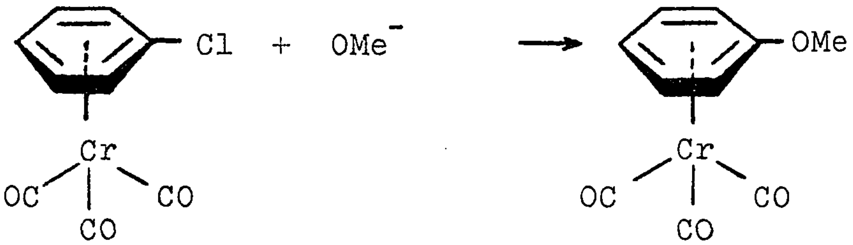
$4s^1 3d^5$ configuration, become nonbonding electrons in d_{xy}, d_{xz}, d_{yz} orbitals on the complexed chromium(0) atom.

Spectral Characteristics

The nmr absorptions of arene protons undergo about 2 δ upfield shift upon complexation to tricarbonylchromium; effects of substituents on arene absorptions are, in general, diminished upon complexation (3, 4, 5, 6), and, in addition, the effect of solvent acetone on the chemical shift of complexed arenes is a different function of substituents than with uncomplexed arenes (7). Strohmeier and Hellman (8) have shown, by dipole moments, that the carbon monoxides are electron rich at the expense of the complexed arene. Furthermore, Fischer (9) and Klopman and Noack (3) have demonstrated that infrared frequencies of the carbon monoxide increase with decreasing electron density on the complexed arene, just as Brown and Sloan (10) predicted.

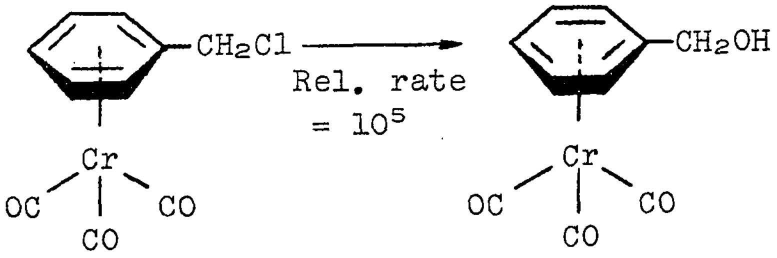
Chemistry

The chemistry of tricarbonylchromium complexes does indeed reflect the highly electron deprived nature of the arene ligand: the rate of basic hydrolysis of substituted (methyl benzoate)tricarbonylchromiums exceeds that for the respective uncomplexed methyl benzoates by a factor of 30-100 times (11); the acidity of (benzoic acid)tricarbonylchromium is almost equal to that for p-nitrobenzoic acid (12); the acidity of (phenylacetic acid)tricarbonylchromium is equal to that for p-nitrophenylacetic acid (13); the acidity of (phenol)tricarbonylchromium is about 3 pK units lower than for phenol (12); the basicity of (aniline)tricarbonylchromium is about 2 pK units higher than for aniline (12); and (phenyl chloride)tricarbonylchromium undergoes facile displacement upon attack with methoxide ion (13).



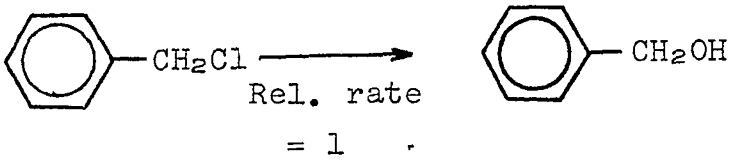
(2)

In spite of the p-nitro-like character of the tricarbonylchromium moiety, the solvolysis of (benzyl chloride)-tricarbonylchromium, 2, is greatly accelerated over the free benzyl chloride. Holmes et al. have suggested that orbitals on chromium(0) are responsible (14) for the presumed stability of (benzyl)tricarbonylchromium cation.



(3)

2

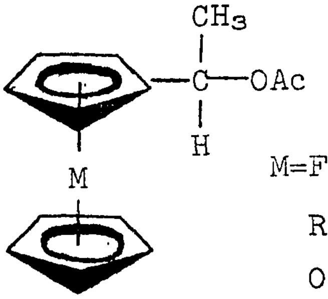


(4)

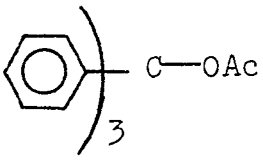
25°

aqueous acetone

The solvolyses of the isoelectronic group V-B metallocenes (15), α-acetoxy ethylcyclopentadienyl, cyclopentadienyl iron, 3, ruthenium, 4, and osmium, 5, are faster than the solvolysis of triphenylmethylacetate, 6, (Table 1).



M=Fe, 3
Ru, 4
Os, 5



6

The stability of the ferrocenylmethyl cation, 7, as reflected in its pK_{R^+} value of -1.28, is much more stable than is predicted from consideration of the rate of

Table 1. Rates of solvolysis of group V-B metallocenyl acetates[a]

Acetate	$k \times 10^5$ [b]
Fc-CH(Me)(OAc)[c]	3.02
Rc-CH(Me)(OAc)[d]	4.14
Oc-CH(Me)(OAc)[e]	18.6
Ph_3COAc	0.34

[a] From reference 15.

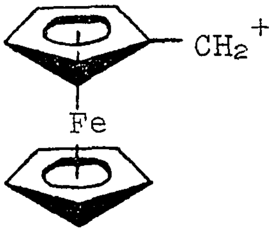
[b] At 15°; in 80% acetone-water; in sec^{-1}.

[c] Fc = 1-cyclopentadienyl, cyclopentadienyl iron.

[d] Rc = 1-cyclopentadienyl, cyclopentadienyl ruthenium.

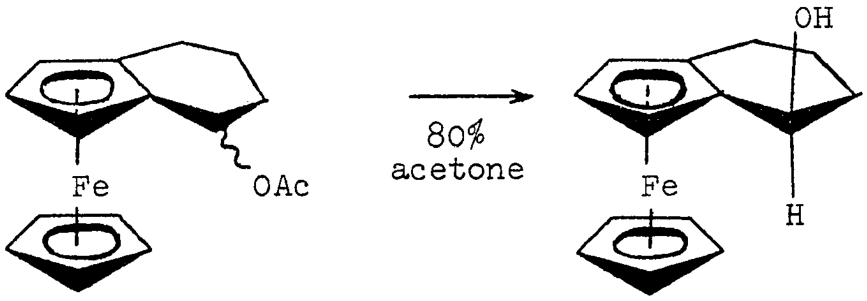
[e] Oc = 1-cyclopentadienyl, cyclopentadienyl osmium.

solvolysis of the corresponding acetate (16). Furthermore the high *exo/endo* ratio (2500) for the solvolytic rates of



7

8 (17), and the almost exclusive formation of exo product (18), 9, have prompted a vigorous debate on the role of the

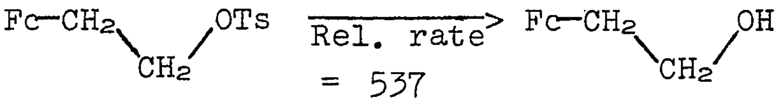


(5)

8 9

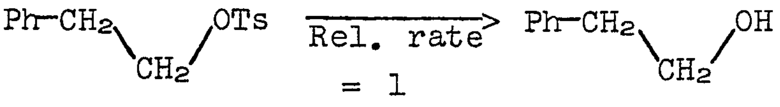
metal in the formation of these stable cations (15, 16, 17, 18, 19, 20, 21, 22).

The β-ferrocenyl group also assists in the formation of cation. The rate of solvolysis of β-ferrocenylethyl tosylate, 10, is 537 times faster than the rate for β-phenethyl tosylate (17).



$$\text{Fc-CH}_2\text{-CH}_2\text{-OTs} \xrightarrow[= 537]{\text{Rel. rate}} \text{Fc-CH}_2\text{-CH}_2\text{-OH} \qquad (6)$$

10



$$\text{Ph-CH}_2\text{-CH}_2\text{-OTs} \xrightarrow[= 1]{\text{Rel. rate}} \text{Ph-CH}_2\text{-CH}_2\text{-OH} \qquad (7)$$

The π-complexed tricarbonylchromium group, if its inductive effect is corrected for, accelerates the solvolysis (23) of 3-phenyl-2-butyl methanesulfonate, particularly if it is *threo*, **11**, (Table 2), but still not near the 537 fold acceleration in the ferrocene system.

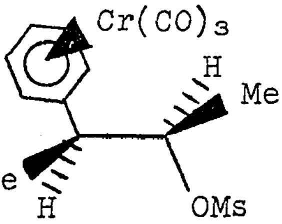


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Table 2. Relative rates of acetolysis of 3-phenyl-2-butyl methanesulfonates and their tricarbonylchromium complexes[a]

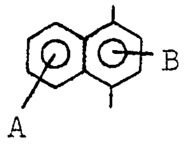
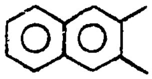
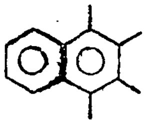
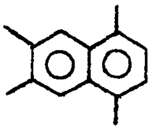
Sulfonate	$k_{relative}$[b]
Erythro	5
Erythro complex	1
Threo	5
Threo complex (**11**)	5

[a] From reference 23.

[b] At 85°; in $\sec^{-1}$.

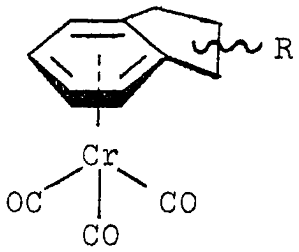
The attachment of the tricarbonylchromium moiety to an aromatic system is sterically sensitive. Deubzer et al. (24) submitted various methylated naphthalenes to complexation (Table 3), concluding that a 1,4-dimethyl group arrangement is less favorable for complexation than is a 1,2-dimethyl arrangement.

Table 3. Complexation of methyl naphthalenes[a]

Arene	Distribution of isomers (%)	
	Ring A	Ring B
	64	36
	25	75
	43	57
	100	0

[a] From Reference 24.

The work of Gracey *et al.* (25) illustrates that the interaction between the tricarbonylchromium group and the



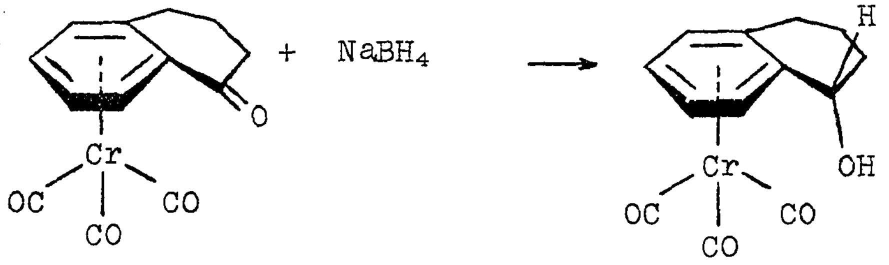
indane 2-substituent is more important than with the 1-substituent (Table 4).

Table 4. The relative stability of geometric isomers of 1- and 2-substituted (indane)tricarbonylchromium[a]

Substituent	*cis*:*trans* ratio 1-substituted	2-substituted
OH	46:54	22:78
Me	53:47	16:84
CO_2Me	57:43	31:69
CN	67:33	30:70

[a] From reference 25.

The hydride reduction of (1-tetralone)tricarbonylchromium gives endo alcohol, meaning that exo approach is involved (26).



(8)

Jackson and Jennings (27) have indicated that a steric effect is responsible for the enhancement of meta-acetylation of alkyl benzenes when they are complexed to tricarbonylchromium (Table 5).

Restricted rotation around the arene-chromium bond, which was at first thought to exist (28), does not, in fact, exist in numerous complexed benzenes substituted with bulky alkyl groups. Indeed, Jula and Seyferth (29) observed only one nmr signal for (1,4-di-trimethylsilyl benzene)tricarbonylchromium, ruling out a preferred (on the nmr time scale) conformation such as **12**, which predicts nonequivalent aromatic protons.

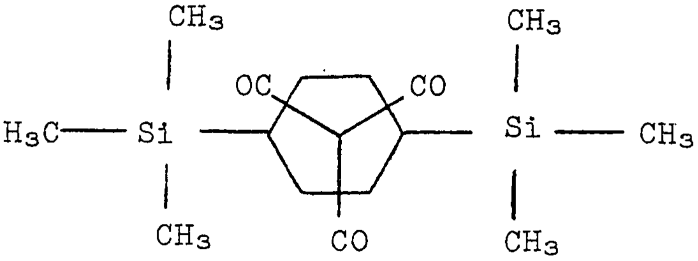


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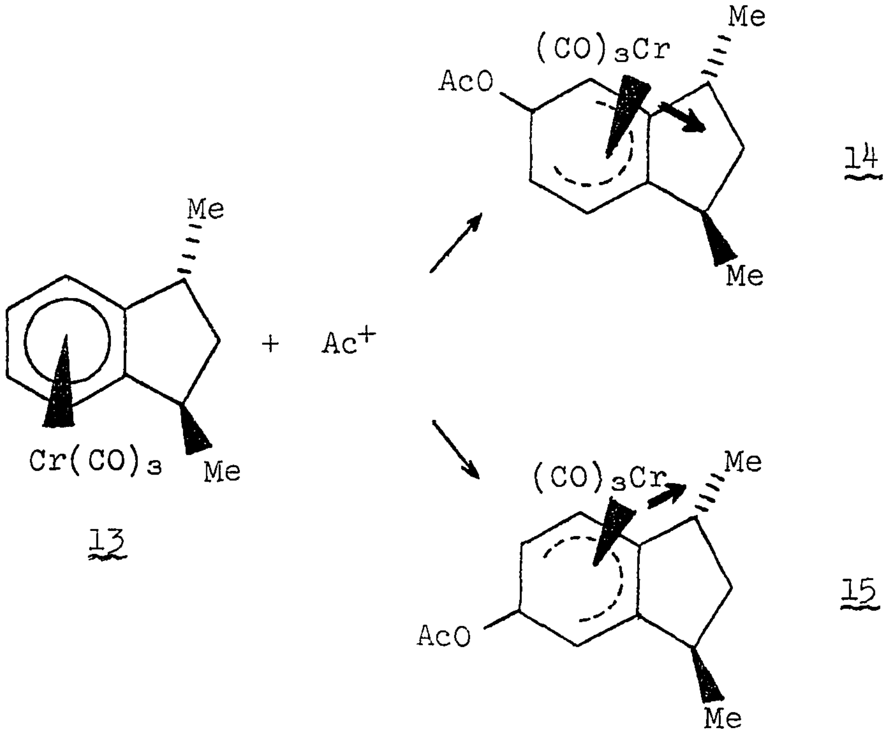
Table 5. Acetylation of alkyl benzenes and their tricarbonylchromium complexes[a]

Benzene substituent	Relative acetylation rates ortho	meta	para
Me	1.2	2	96.8
Me; $Cr(CO)_3$	43	17	40
Et	0.4	2.9	96.7
Et; $Cr(CO)_3$	24	33	43
i-Pr	0.1	3.4	96.5
i-Pr; $Cr(CO)_3$	5	59	36
t-Bu	0	4.3	95.7
t-Bu; $Cr(CO)_3$	0	87	13

[a] From reference 27.

Gracey et al. (30) observed preferential acetylation of (1,3-trans-dimethyl indane)tricarbonylchromium, 13, and they leaned toward the explanation that 5-acetylation would give an intermediate in which the tricarbonylchromium is close to the 3-methyl, 14, whereas 6-acetylation, 15, involves no such steric interaction.

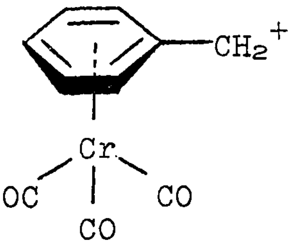


(9)

CHAPTER II. INTRODUCTION

The rate of solvolysis of (benzyl chloride)tricarbonylchromium, 2, has led to the presumption that the complexed benzyl cation is extraordinarily stable (Equations 3 and 4).

It is not clear what factors are responsible for the apparent stability of the (benzyl)tricarbonylchromium cation, 16. This work will demonstrate the unique effects



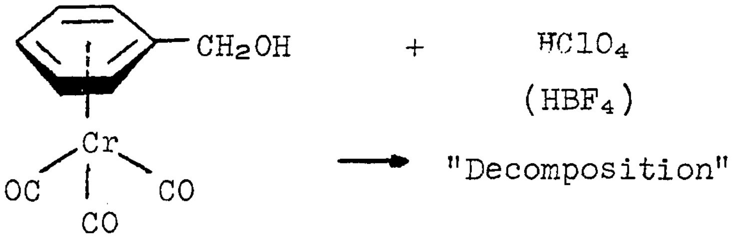
16

of the tricarbonylchromium substituent upon electron deficient centers. We shall propose and substantiate mechanisms that could be responsible for the remarkable stability of the (benzyl)tricarbonylchromium cation.

CHAPTER III. RESULTS AND DISCUSSION

Formation and Stability of (Benzyl)tricarbonylchromium Cation

Holmes _et_ _al_. maintained that attempts to form salts of the alledgedly stable (benzyl)tricarbonylchromium cation were foiled by facile decomposition. Thus treatment of (benzyl alcohol)tricarbonylchromium, 17, with perchloric acid, fluoroboric acid, and treatment of the chloride with silver perchlorate ended in decomposition (14).



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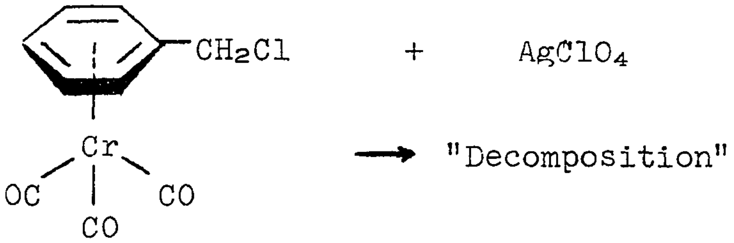
(10)



2

(11)

We have found that if an ethanolic or acetic acid solution of a number of substituted (benzyl alcohol)tricarbonylchromiums is injected into rapidly stirring, nitrogen-saturated, sulfuric acid, a specie possessing new spectral absorptions can persist for several seconds (Table 6).

Table 6. Spectra of substituted (benzyl alcohol)tricarbonylchromiums[a]

p-Substituent	95% EtOH	41% H_2SO_4	85-87% H_2SO_4
H (17)	2170(25800)[b] 2540(6410) 3155(9650)	2160(26600) 2530(6020) 3130(9800)	2010(27800) 2780(11500) 3480(1500) 5135(365)
Me (18)	2180(24300) 2540(6300) 3160(9610)	2170(23600) 2530(5110) 3110(7660)	2060(25000) 2450(8790) 2800(11850) 3490(1070) 5400(380)
MeO (19)	2100(31900) 2540(6240) 3170(9150)	2090(28400) 2530(4980) 3110(7050)	2260(22200) 2860(11330) 3480(1440) 5130(450)
Cl (20)	2150(26900) 2590(8450) 3190(10900)	2140(25500) 2530(8410) 3180(9030)	2185(23600) 2840(6270) 2680(7980) 5300(355)

[a] All absorptions are given in Angstroms and the molar extinction coefficients are parenthesized.

[b] According to Ercoli and Mangini (31), the absorptions for (benzyl alcohol)tricarbonylchromium are λ_{max} 2180 (23500), 2500 (7110), and 3150 (9350).

The formation of the new specie is reversible as shown by the following recovery experiments.

(A) When a solution of (benzyl alcohol)tricarbonylchromium in 83% sulfuric acid (violet) is poured onto ice to give a 53% sulfuric solution (yellow), the spectrum is as follows: λ_{max} 2140 (26200), λ_{max} 2520 (5700), λ_{max} 3120 (11400). Comparison with the values in 41% sulfuric acid (Table 6) shows that, within 20 Angstroms and about 10% in absorbance, the spectrum is identical to that of the complexed alcohol.

(B) When a solution of the (benzyl alcohol)tricarbonylchromium, 17, in 85% sulfuric acid (violet) was poured onto ice, the characteristic yellow color of the alcohol was produced, and workup gave a 58% isolated (77% by nmr on the crude product) recovery of the starting material (verified by melting point, mixed melting point, and nmr). This is, indeed, a low recovery, but an attempt to isolate (p-methylbenzyl alcohol)tricarbonylchromium, 18, from 51% sulfuric acid (in which it is in the alcohol form) gave a mere 63% isolated recovery of the alcohol. Therefore, we believe that acid oxidation of the alcohol is sufficient to account for the low recovery of the alcohol from the concentrated acid solutions.

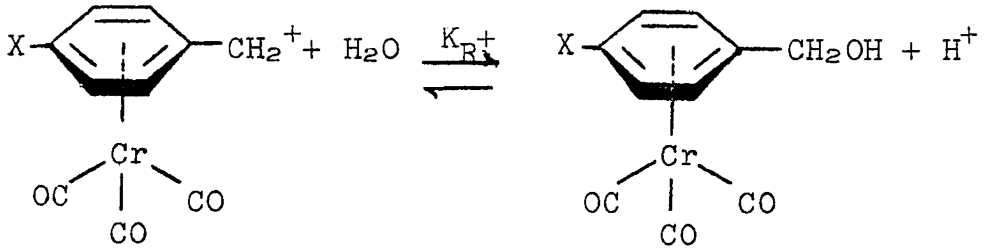
The spectrum of (benzene)tricarbonylchromium, 1, undergoes only small hypsochromic shifts upon dissolution in progressively stronger sulfuric acids (Table 7). This behavior is in contrast to that of the benzyl alcohols where bathochromic shifts are extensive.

Table 7. Spectra of (benzene)tricarbonylchromium in ethanol and sulfuric acids[a]

95% EtOH	41% H_2SO_4	85%H_2SO_4	97%H_2SO_4
2170(30300)	2170(24500)	2030(16100)	2010(17600)
2530(8800)	2530(5810)	2480(4540)	2480(5190)
3130(11300)	3090(8500)	2980(2120)	2910(2670)

[a] All absorptions are given in Angstroms and the molar extinction coefficients are parenthesized.

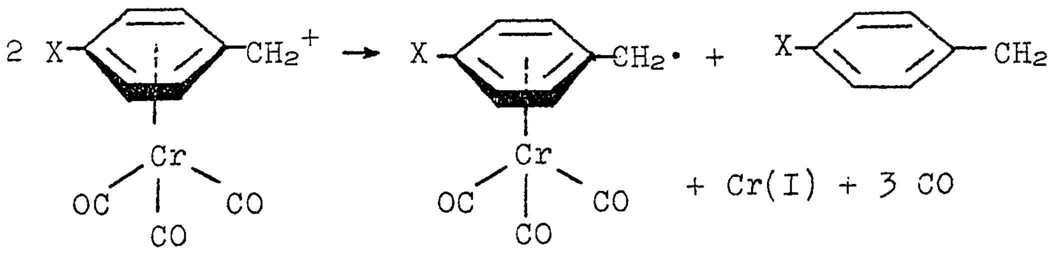
Thus we believe the spectral changes (Table 6) demonstrate establishment of the complexed benzyl cation-



(12)

alcohol equilibrium.

The spectral absorptions do eventually decay and the recovered product of the decomposition is the bis-[(benzyl)-tricarbonylchromium], 21. Moreover, the rate of decomposition is much faster in solutions containing a high stoichiometric concentration of alcohol. We favor the following description of the decay process.



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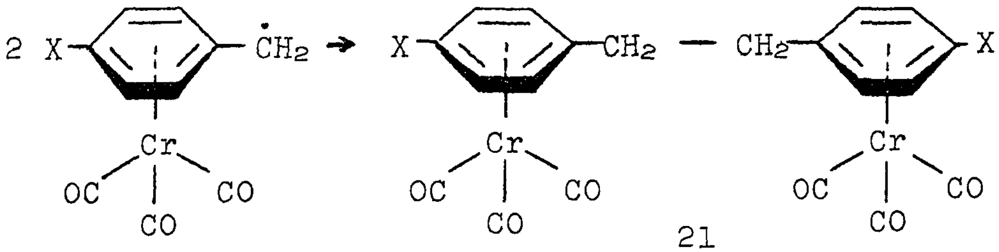


(14)

21

The quantitative measurement of the stability of the (benzyl)tricarbonylchromium cation is reflected in the value of K_{R^+} for Equation 12. Deno has defined a "C_o" acidity function (32) in terms of the ratio of the concentration of cation, R^+, and its conjugate base, ROH, and the "C_o" value for the particular sulfuric acid concentration employed. The quotient term is obtained spectrophotometrically. The

$$-\log K_{R^+} = p\underline{K}_{R^+} = C_o + \log([R^+]/[ROH]) \qquad (15)$$

C_o values for various sulfuric acid-water mixtures are tabulated in the literature (32). The usual procedure is to plot an absorption of the cation that is free from interference by alcohol absorption against C_o; at the inflection (where it can be shown (33), $[R^+] = [ROH]$), the absorption should be $\frac{1}{2}$ the value for 100% cation (very strong acid solution), and the corresponding C_o value is taken as the pK_{R^+} of the cation. A typical plot, that for (benzyl)tricarbonylchromium cation is shown (Figure 1).

Para-substituent effects

There exists a good linear free energy relationship between pK_{R^+} of four *para*-substituted complexed benzyl alcohols (Table 8) and σ (Figure 2), $\rho = -5.1 \pm 0.5$, but not with σ^+ (Figure 3), $\rho^+ = -2.7 \pm 0.6$.

Table 8. The pK_{R^+} values of *p*-substituted (benzyl)tricarbonylchromium cations

p-Substituent	pK_{R^+}
H (**16**)	-11.8
Me (**22**)	-11.0
Cl (**23**)	-12.8
OMe (**24**)	-10.2

Figure 1. The molar extinction coefficient of (benzyl)tricarbonylchromium cation at 5135 Å *vs.* the C_0 of the sulfuric acid-water solvent

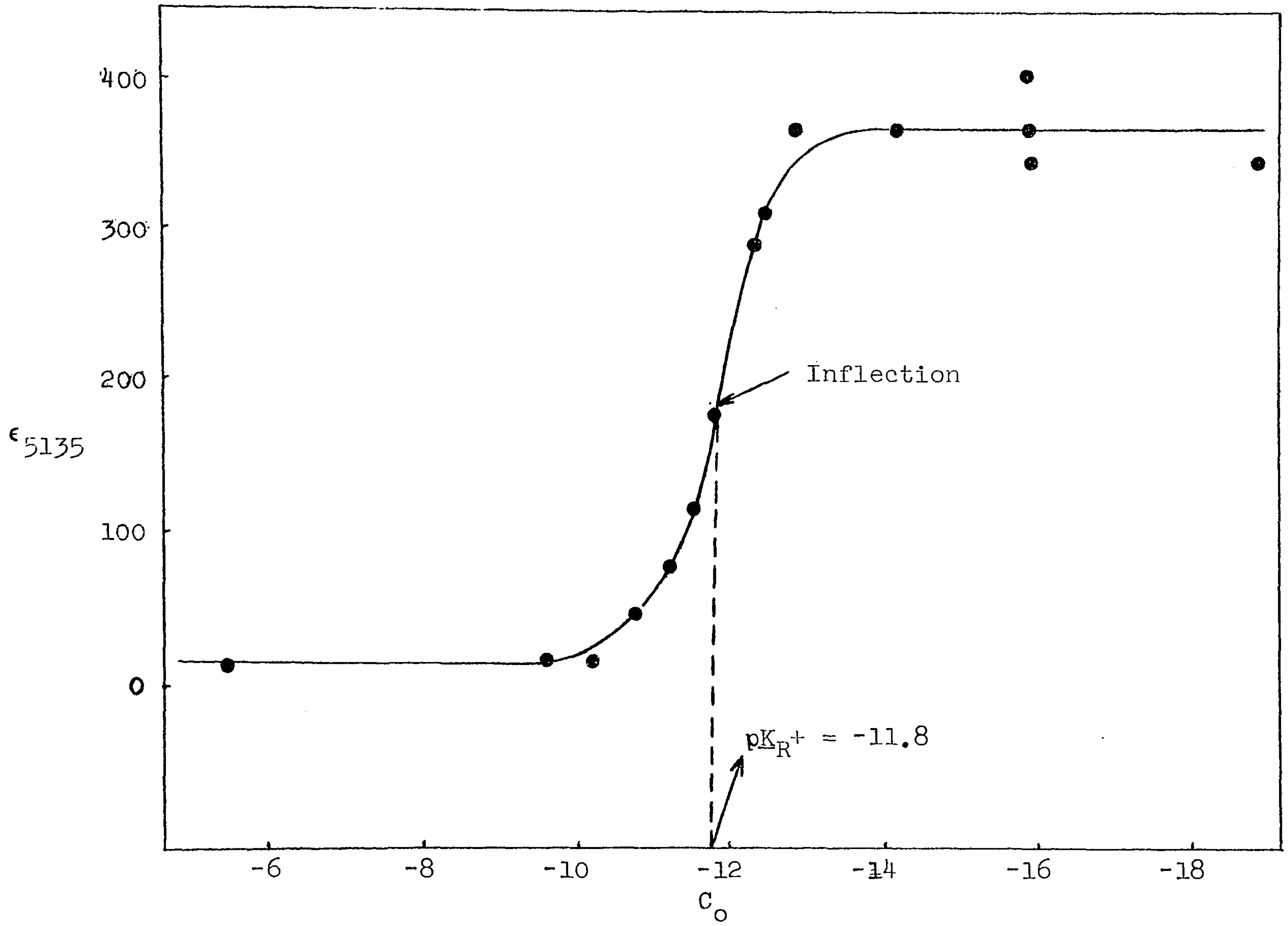

400
300
200
100
0
ϵ_{5135}
Inflection
$p\underline{K}_{R^+} = -11.8$
-6
-8
-10
-12
-14
-16
-18
C_o

Figure 2. The pK_{R^+} of p-substituted (benzyl)tricarbonylchromium cations vs. σ of the p-substituent

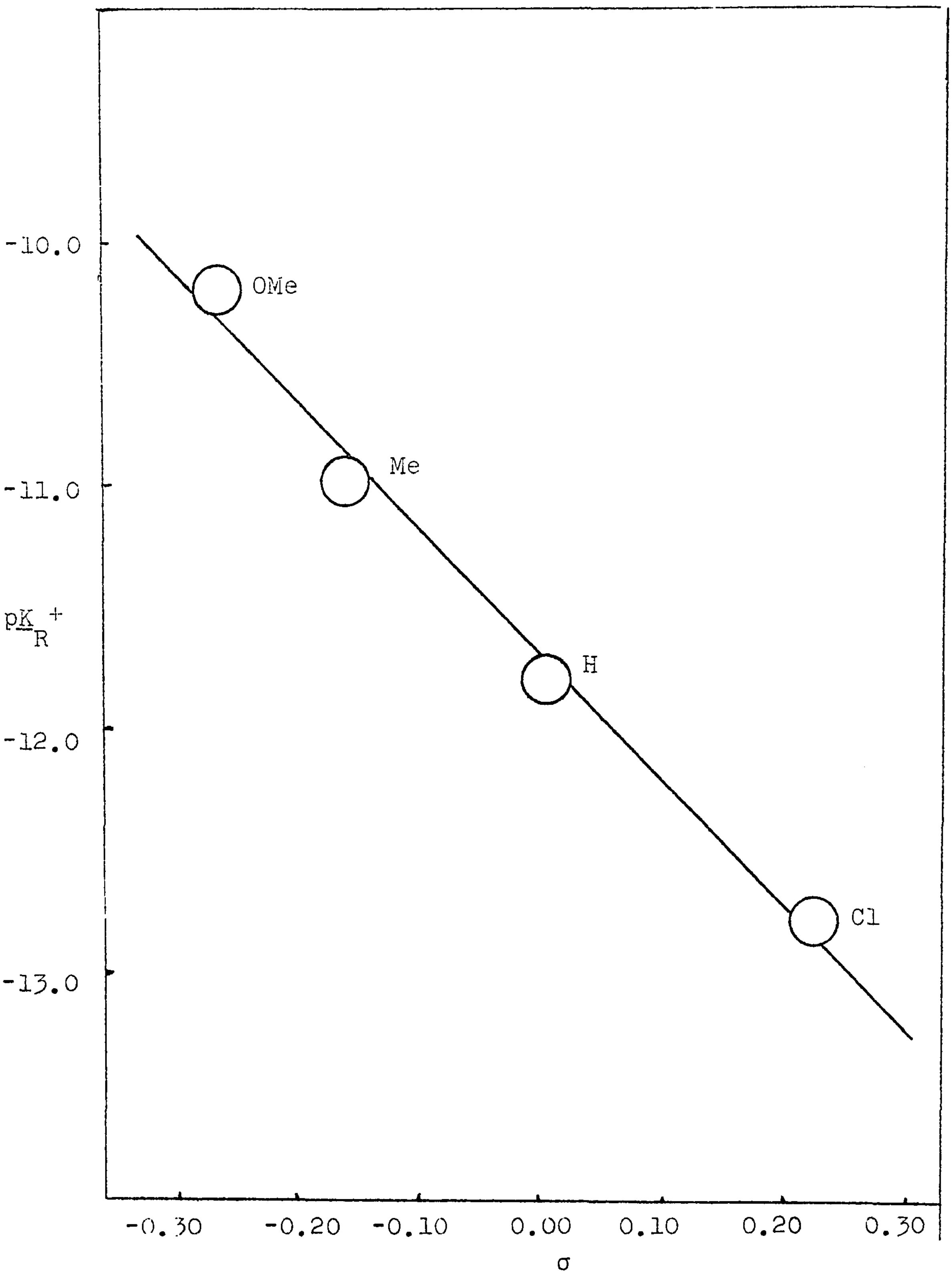

-10.0
-11.0
-12.0
-13.0
pK_{R^+}
OMe
Me
H
Cl
-0.30
-0.20
-0.10
0.00
0.10
0.20
0.30
σ

Figure 3. The $p\underline{K}_{R^+}$ of p-substituted (benzyl)tricarbonylchromium cations vs. σ^+ of the p-substituents

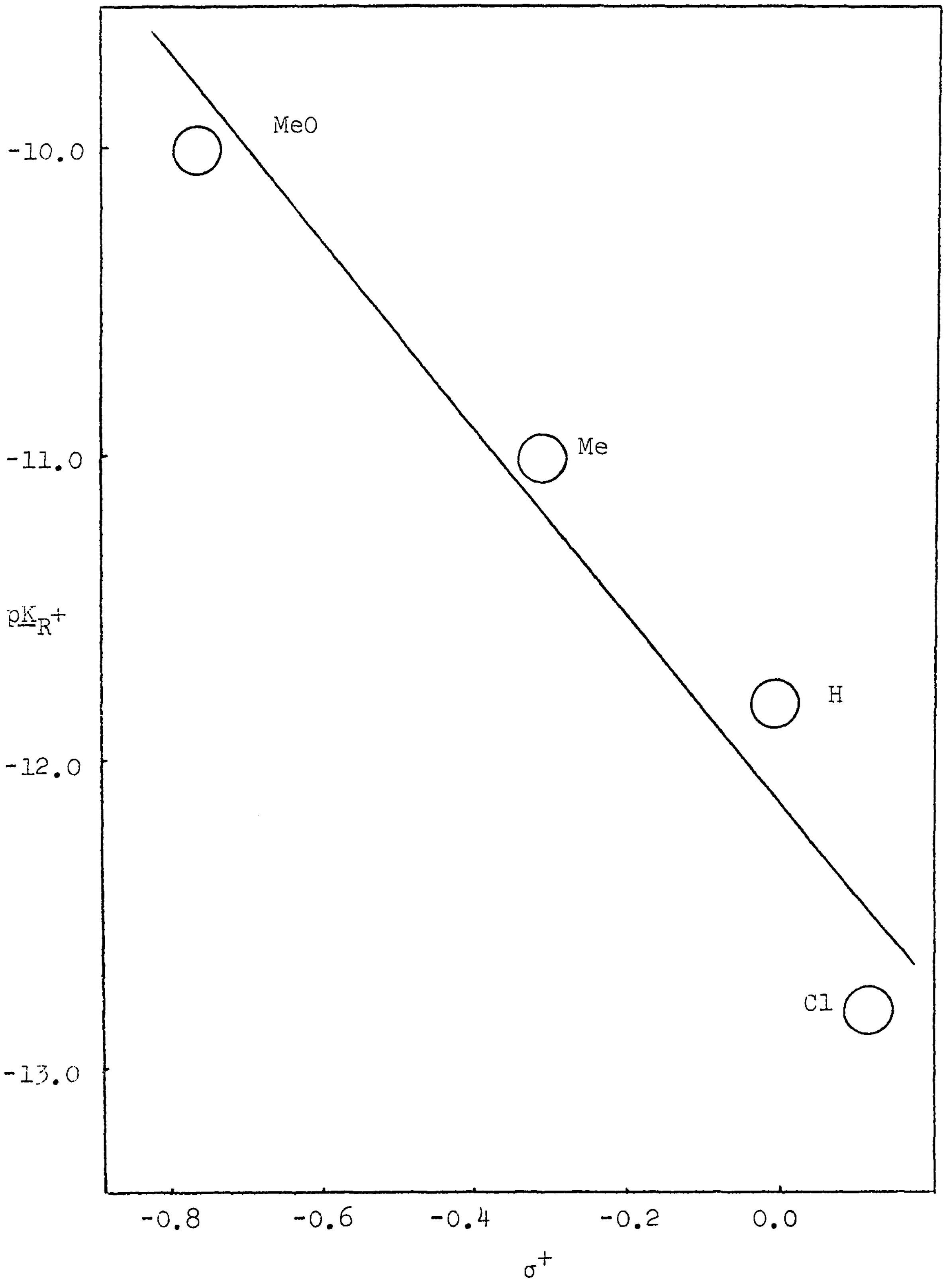

MeO
Me
H
Cl
-10.0
-11.0
-12.0
-13.0
$p\underline{K}_{R^+}$
-0.8
-0.6
-0.4
-0.2
0.0
σ^+

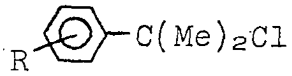
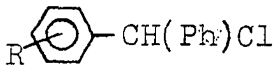
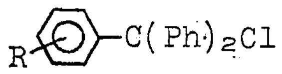
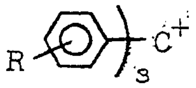
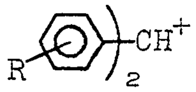
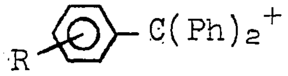
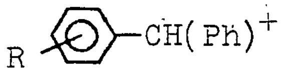
Table 9 lists ρ's for the triply substituted triphenylmethyl cation, 25, the doubly substituted diphenylmethyl cation, 26, the monosubstituted triphenylmethyl cation, 27, the monosubstituted diphenylmethyl cation, 28, and for the solvolysis of substituted cumyl chlorides, benzhydryl chlorides, and triphenylmethyl chlorides.

Even though 1/3 of the positive charge is affected by each ring-substituent in 25, and 1/2 of the positive charge is affected by each ring-substituent in 26, the ρ values are nearly the same, -11.9 and -11.4, because the number of substituents is different by that same ratio, 3/2; i.e., the effect by the sum of the ring-substituents, the ρ value, is a product of the sensitivity to one ring-substituent times the number of ring-substituents.

If the ρ value for 27 is multiplied by three, the result, -10.8, is nearly equal to ρ for the tri-substituted cation, 25. Similarly, if the ρ value for 28 is multiplied by two, the result, -11.0, is nearly equal to the ρ value for 26.

Furthermore, the ratio of the ρ values of 27 and 28 is equal to the inverse ratio of respective number of phenyl rings in the system; i.e., substitution of a phenyl ring onto 28 decreases ρ by 2/3. Conversely, removing a phenyl group from 28 should increase ρ by 2/1. This means that the ρ for ring-substituted benzyl cations is -11, very

Table 9. The ρ for the substituent effects upon the stability of cations or upon the rate of formation of cations

Reaction or Cation	ρ
Hydrolysis of 	-4.6[a]
Alcoholysis of 	-3.7[b]
Alcoholysis of 	-3.5[b]
 (25)	-11.9[c]
 (26)	-11.4[c]
 (27)	-3.6[d]
 (28)	-5.5[c]

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[a] Reference 34.

[b] Calculated by Deno and Evans (35).

[c] Reference 35.

[d] Calculated from the data of Deno and Evans.

much in agreement with what one would expect from extrapolation of systems **25** and **26** to a benzyl system.

Therefore the tricarbonylchromium group must be, in some way, responsible for the very much lower ρ in the (benzyl)tricarbonylchromium cation. This fact, in addition to the better fit with σ (Figure 2), strongly implies that the metal is absorbing a large amount of the positive charge on the benzylic carbon.

Stability of the (benzyl)tricarbonylchromium cation relative to other cations

The complexed benzyl cation, **16**, is slightly more stable (relative to the alcohol) than the free diphenylmethyl cation, **29**, as one would expect from a comparison of the solvolysis rates of the two chlorides (Table 10). Because the $p\underline{K}_{R^+}$ of the free benzyl cation, **30**, is not firmly established, we include, for the sake of comparison with uncomplexed cation stability, the $p\underline{K}_{R^+}$ value of the free, **31**, and complexed mesityl cation, **32**; the 8 $p\underline{K}_{R^+}$ units difference corresponds to a 11 kcal/mole stabilization of this cation by virtue of the attachment to a tricarbonylchromium group.

The effect of complexed tricarbonylchromium upon the stability of a very stable cation, the tropylium ion, is small (14), not near the > 7 $p\underline{K}_{R^+}$ units in the benzyl cation case (Table 11).

Table 10. The pK_{R^+} values of various carbonium ions and rates of solvolysis of the corresponding aralkyl chlorides in aqueous acetone

Carbonium ion	pK_{R^+}	$k_{relative}$
Ph_3C^+	-6.6[a]	2.2×10^9 [b]
π-$(PhCH_2)[Cr(CO)_3]^+$ (16)	-11.8[c]	2.2×10^5 [d]
Ph_2CH^+ (29)	-13.3[e] -13.4[c]	6.9×10^4 [d]
$PhCH_2^+$ (30)	< -17.3[e]	1.00[d]
2,4,6-$(CH_3)_3C_6H_2CH_2^+$ (31)	-17.3[e] -17.0[c]	
π-(2,4,6-$(CH_3)_3C_6H_2CH_2)[Cr(CO)_3]^+$ (32)	-9.3[c,f]	

[a] Reference 32.

[b] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, 1962.

[c] This study.

[d] Reference 14.

[e] N. C. Deno, P. F. Groves, J. J. Jaruzelski, and M. N. Lugasch, J. Am. Chem. Soc., 82, 4719 (1960).

[f] Visible absorption at 5150 Å (extinction coefficient 500).

Table 11. The pK_{R^+} values for tropylium ion and (tropylium)-tricarbonylchromium cation[a]

Carbonium ion	pK_{R^+}
$C_7H_7^+$	4.7
π-$(C_7H_7)[Cr(CO)_3]^+$	6.3

[a]From reference 14.

The Electronic Behavior of the Tricarbonylchromium Moiety

In the solvolysis reaction

Complexed benzyl chloride, 2, solvolyzes 2.2 x 10^5 times faster than benzyl chloride in 80% acetone-water (14). The ρ for benzyl chlorides is a function of the aromatic substituent (a change of mechanism is responsible); it is -1.4 from the p-nitro and p-hydrogen rates and -3.8 from p-hydrogen and p-methyl rates (36). The ρ for α-methylbenzyl chlorides and cumyl chlorides is -4.03 (37) and -4.6 (34), respectively. We estimate, then, that the ρ for the benzyl chloride solvolysis in the range of substituents from p-hydrogen to tricarbonylchromium is -3.5 ± 1.0. The calculated σ^+ for tricarbonylchromium in the solvolysis reaction is then obtained from Equation 16.

$$\sigma^{+} = (\log (k/k_o))/\rho$$
$$= \log (2 \times 10^{5}/(-3.5 \pm 1.0)) = 1.54 \pm 0.40 \qquad (16)$$

We shall define the effective substituent parameter, σ^{+}, to be equal to the sum of the inductive parameter, σ^{o}, and a release parameter, σ_{A}^{+}. For the tricarbonylchromium

$$\sigma^{+} = \sigma^{o} + \sigma_{A}^{+} \qquad (17)$$

substituent, $\sigma^{o} = 0.82$ (13). Therefore, rearrangement of Equation 17 and substitution gives,

$$\sigma_{A}^{+} = (-1.54 \pm 0.40) - 0.82 = -2.36 \pm 0.40 \qquad (18)$$

so that, in the solvolysis reaction, tricarbonylchromium is more electron donating to electron deficient centers than is any "normal" substituent.

In benzoyl compounds

The electronegativity of the tricarbonylchromium group The ir data on complexed benzoyl moieties, π-(PhCOR)Cr(CO)$_3$, indicate that the tricarbonylchromium group does not always possess such a highly negative σ^{+} (or σ_{A}^{+}) value as it does in solvolysis.

The rates of solvolysis of alkyl tosylates R_2CHOTs have been quantitatively correlated with the carbonyl stretching frequencies in the corresponding ketone, R_2CO, (38, 39) (the faster the solvolysis, the lower the carbonyl frequency). A similar correlation exists for the aralkyl chlorides (ArCHMeCl) and the carbonyl frequencies of the respective aryl methyl ketones (ArCOMe) (19). From the plot of σ^+ of p-substituted aryl alkyl ketones vs. the respective carbonyl frequencies, ν_{CO}, Traylor and Ware have shown that the σ^+ for the ferrocenyl group (isoelectronic to (phenyl)tricarbonylchromium), in ferrocenyl methyl ketone ($\sigma^+ = -1.3$) corresponds quite closely to the σ^+ obtained from the comparison of α-methylferrocenyl carbinyl and α-methylbenzyl chloride solvolysis rates ($\sigma^+ = -1.3$) (19).

Analogously then, if the accelerated rate of (benzyl chloride)tricarbonylchromium, 2, over the free benzyl chloride is due to electron delocalization onto the α-carbonium ion, the carbonyl stretching frequency, ν_{CO}, of the complexed aryl methyl ketone, 33, which should be similarly dependent on σ^+, should be less than that for the uncomplexed aryl methyl ketone, 34. From Table 12, just the opposite is true, indicating that, in this ketone, the tricarbonylchromium substituent is electron withdrawing compared to hydrogen.

Variable electron release Why does not that tricarbonylchromium inductive effect which we have invoked to explain the (acetophenone) ir data account for its electron releasing behavior in the benzyl carbonium ion (formed in solvolysis) system? In fact, the net electron release of the complexed arene into the adjacent carbonyl of benzoyl compounds, π-(PhCOR)Cr(CO)$_3$, can indeed approach that displayed in the carbonium ion system: the effect of the tricarbonylchromium depends upon the electronic nature of the carbonyl substituent, R (Table 12).

The carbonyl stretching frequency change upon complexation, $\Delta \nu_{CO}$, correlates better with σ_p^+ (Figure 4) of the carbonyl substituent than with σ_p (Figure 5), or σ_m (Figure 6), even though the stretching frequency of both the free (40) and complexed benzoyl compounds follow σ_m (when the carbonyl substituent is phenyl, i.e., benzophenone, resonance effects become overriding (40)) (Figures 7 and 8).

The uniqueness of the tricarbonylchromium group will be shown by a demonstration of its ability to undergo a change in σ^+ as a function of the electronic nature of the carbonyl substituent, R, in various benzoyl compounds, π-(PhCOR)Cr(CO)$_3$. Of course, the σ^+ for a "normal" substituent would maintain the same value whether the carbonyl substituent was hydrogen, methyl, methoxy, etc.

Table 12. The carbonyl stretching frequencies of benzoyl systems and their tricarbonylchromium complexes

Compound[a]	ν_{CO}[b,c]
PhCHO (35)	1705.8
π-(PhCHO)Cr(CO)$_3$ (36)	1700.3
PhCOMe (34)	1687.8
π-(PhCOMe)Cr(CO)$_3$ (33)	1686.6
PhCO$_2$Me (37)	1732[d]
π-(PhCO$_2$Me)Cr(CO)$_3$ (38)	1732[d]
PhCOAz[e] (39)	1678.4
π-(PhCOAz)Cr(CO)$_3$[e] (40)	1681.5
PhCONMe$_2$ (41)	1630.8
π-(PhCONMe$_2$)Cr(CO)$_3$ (42)	1638.8
p-NO$_2$PhCONMe$_2$ (43)	1638.1

---

[a] All solutes 0.038-0.039 M in chloroform.

[b] Frequencies in wave numbers.

[c] Estimated maximum error ± 1 cm^{-1}.

[d] From reference 3.

[e] "Az" = 1-aziridinyl.

Table 12 (Cont.)

Compound[a]	ν_{CO} [b,c]
$PhCOCH{=}CHNMe_2$ (44)	1554.8
π-$(PhCOCH{=}CHNMe_2)Cr(CO)_3$ (45)	1565.2
Ph_2CO (46)	1661.8
π-$(Ph_2CO)Cr(CO)_3$ (47)	1662.7
$PhCO_2H$ (48)	1699.5
π-$(PhCO_2H)Cr(CO)_3$ (49)	1711.7

From the carbonyl frequencies of the benzoyl system, PhCOR, there exist, in chloroform solution, carbonyl frequencies for R = hydrogen, methyl, ethoxide (41, 42), hydroxide (43), and R = phenyl (41, 42, 44). These frequencies can be correlated with σ^+ of the p-substituent as Traylor and Ware (19) have shown in the acetophenones (in carbon tetrachloride solution), as Stewart and Yates (43) have shown in the benzophenones. Figure 9 demonstrates the aptness of the σ^+ parameter. We may plot a two point line using our frequencies for N,N-dimethylbenazmide (41) and p-nitro N,N-dimethylbenzamide (43) (Figure 9).

So that for six benzoyl systems, determination of the σ^+ for the tricarbonylchromium group is a simple matter of picking off the plot the σ^+ corresponding to the respective

Figure 4. The increase of carbonyl stretching frequency of benzoyl systems upon complexation, $\Delta\nu_{CO}$, *vs*. σ_p+ of the carbonyl substituent

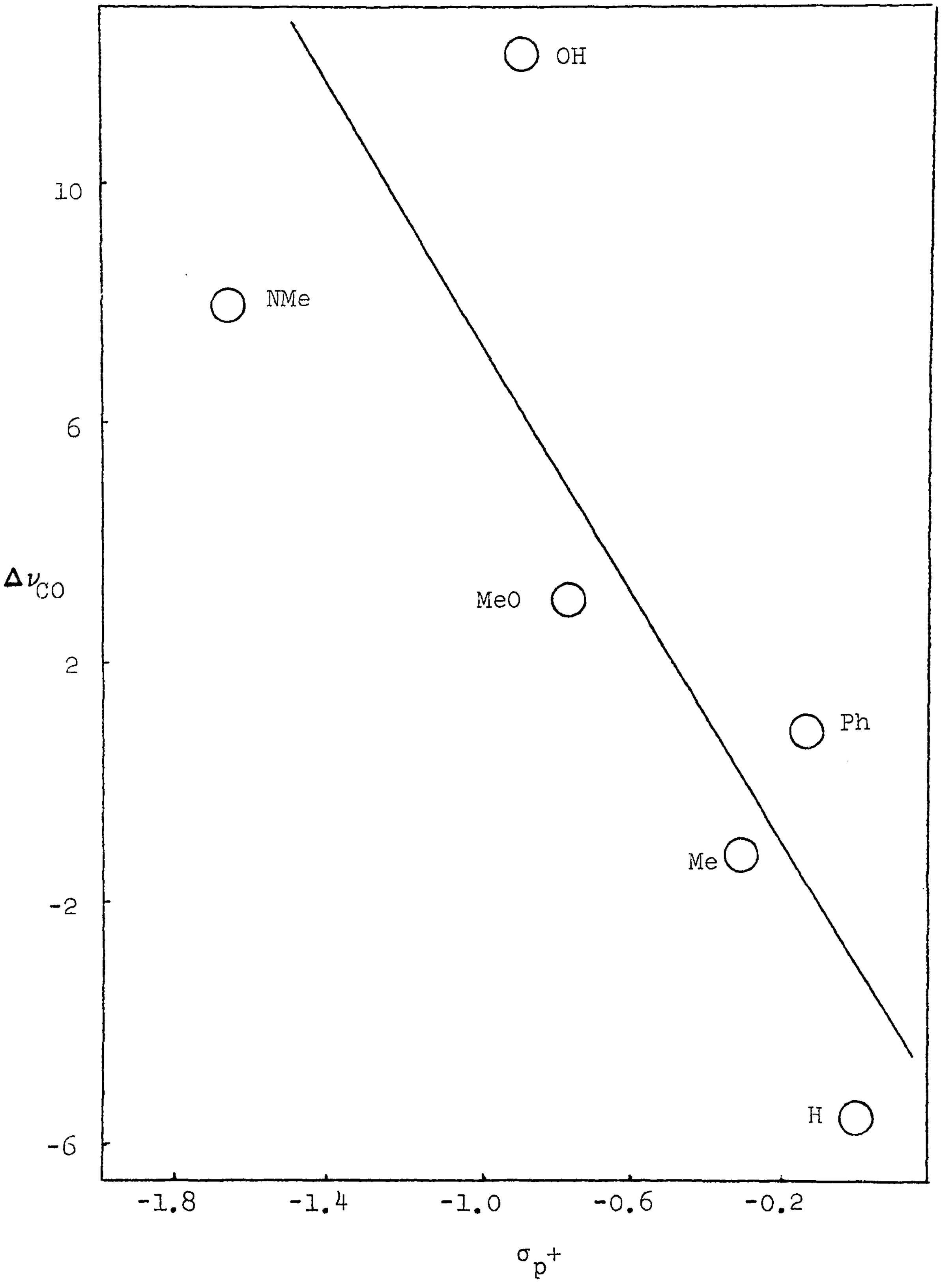

OH
NMe
MeO
Ph
Me
H
10
6
2
-2
-6
$\Delta\nu_{CO}$
-1.8
-1.4
-1.0
-0.6
-0.2
σ_p^+

Figure 5. The increase of carbonyl stretching frequency of benzoyl systems upon complexation, $\Delta\nu_{CO}$, *vs*. σ_p of the carbonyl substituent

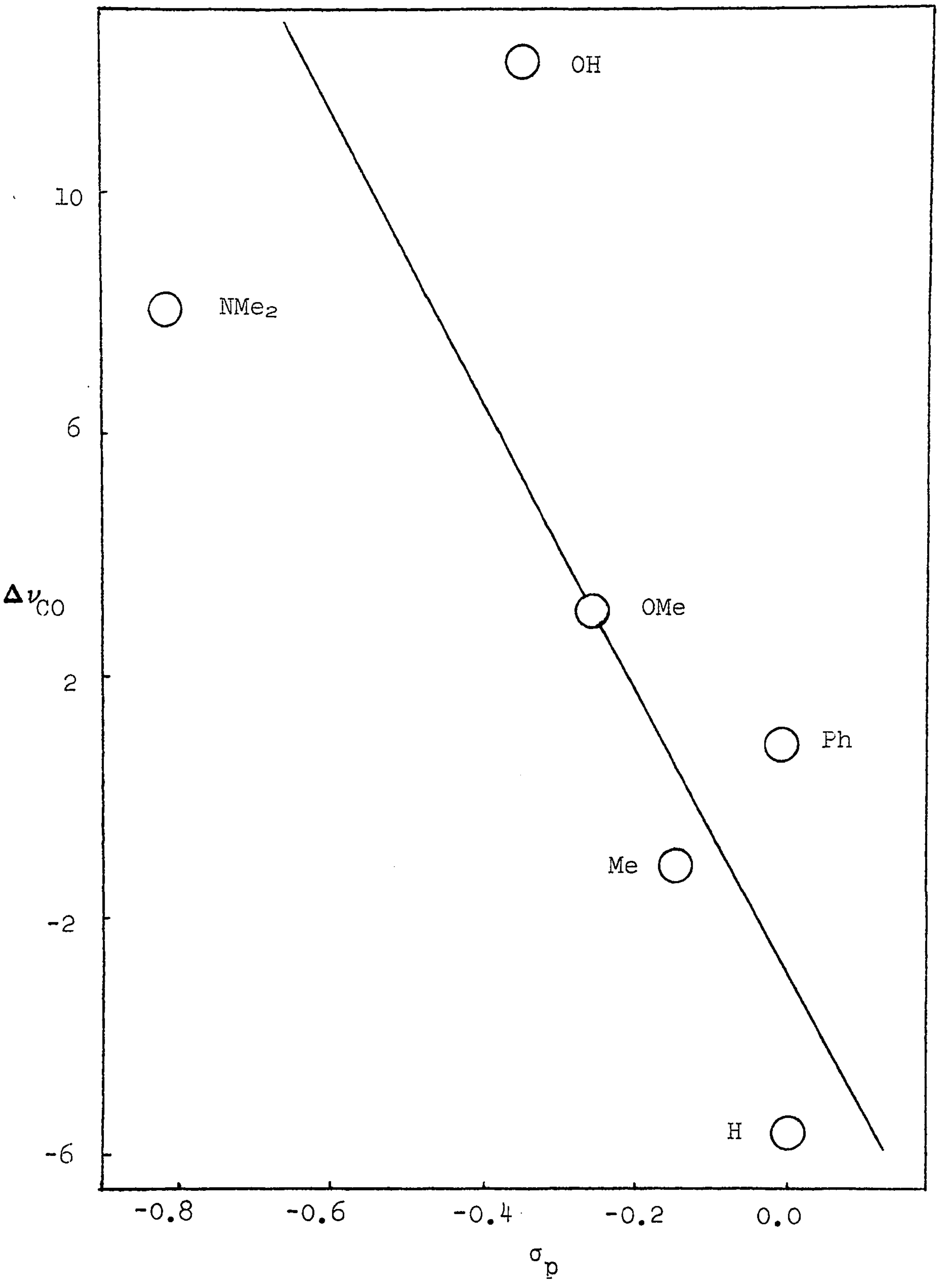

OH
10
NMe2
6
Δν_CO
OMe
2
Ph
Me
-2
H
-6
-0.8
-0.6
-0.4
-0.2
0.0
σ_p

Figure 6. The increase of carbonyl stretching frequency of benzoyl systems upon complexation, $\Delta\nu_{CO}$, *vs.* σ_m of the carbonyl substituent

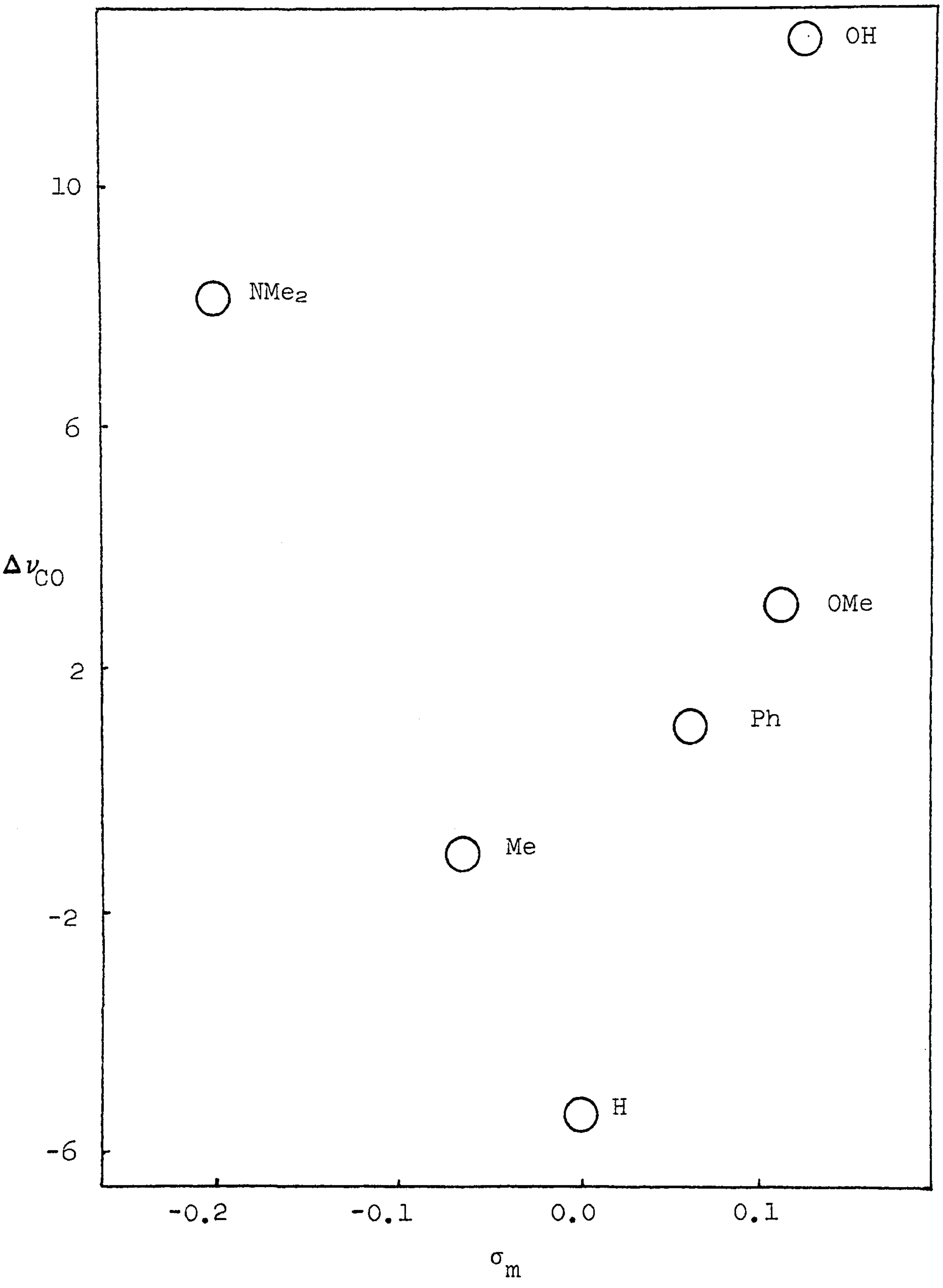

OH
NMe₂
OMe
Ph
Me
H
10
6
2
-2
-6
Δν_CO
-0.2
-0.1
0.0
0.1
σ_m

Figure 7. The carbonyl stretching frequencies of complexed benzoyl systems, ν_{CO}, vs. σ_m of the carbonyl substituent

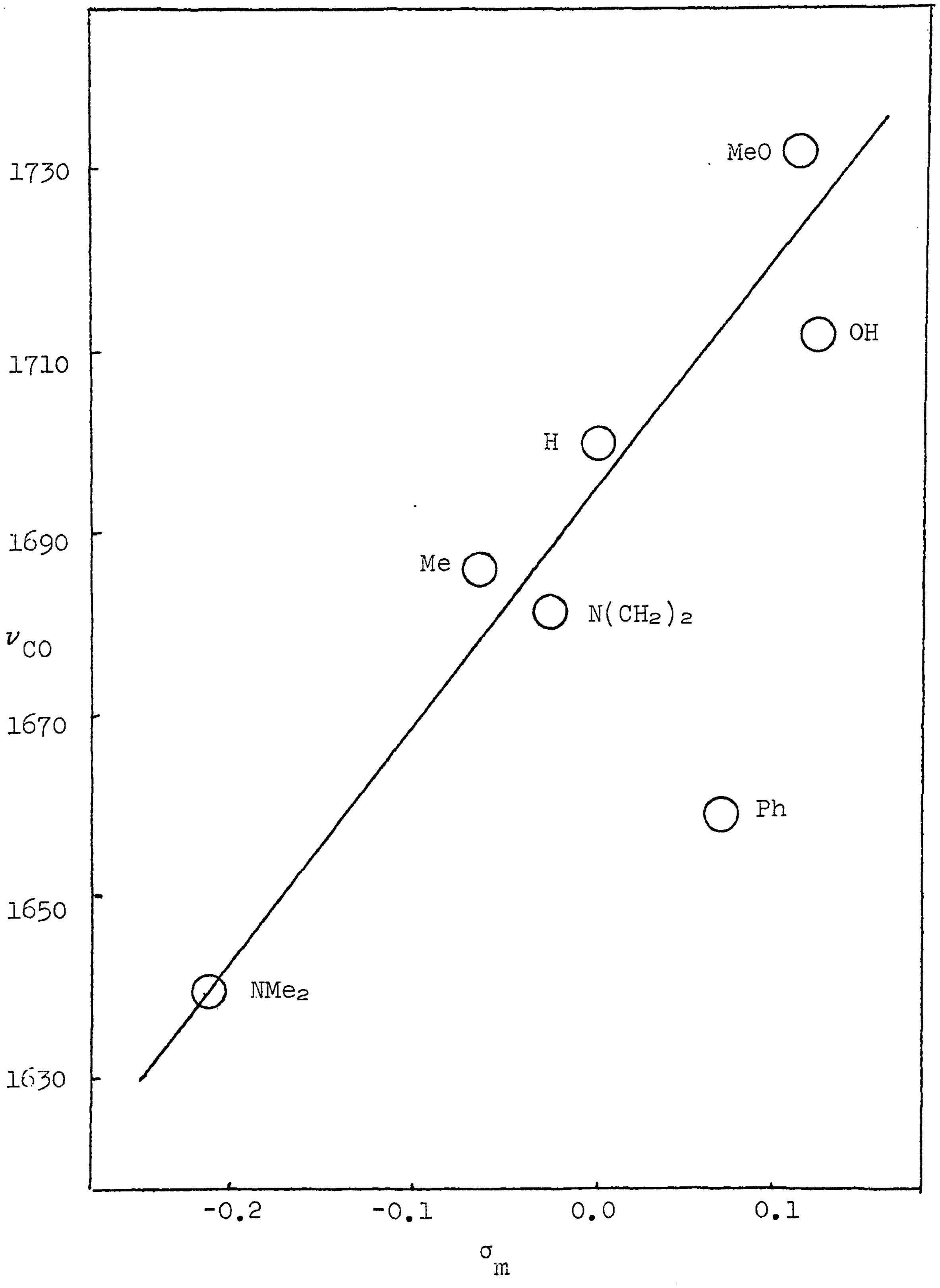

1730
1710
1690
1670
1650
1630
ν_{CO}
-0.2
-0.1
0.0
0.1
σ_m
MeO
OH
H
Me
N(CH₂)₂
Ph
NMe₂

Figure 8. The carbonyl stretching frequencies of benzoyl systems, ν_{CO}, vs. σ_m of the carbonyl substituent

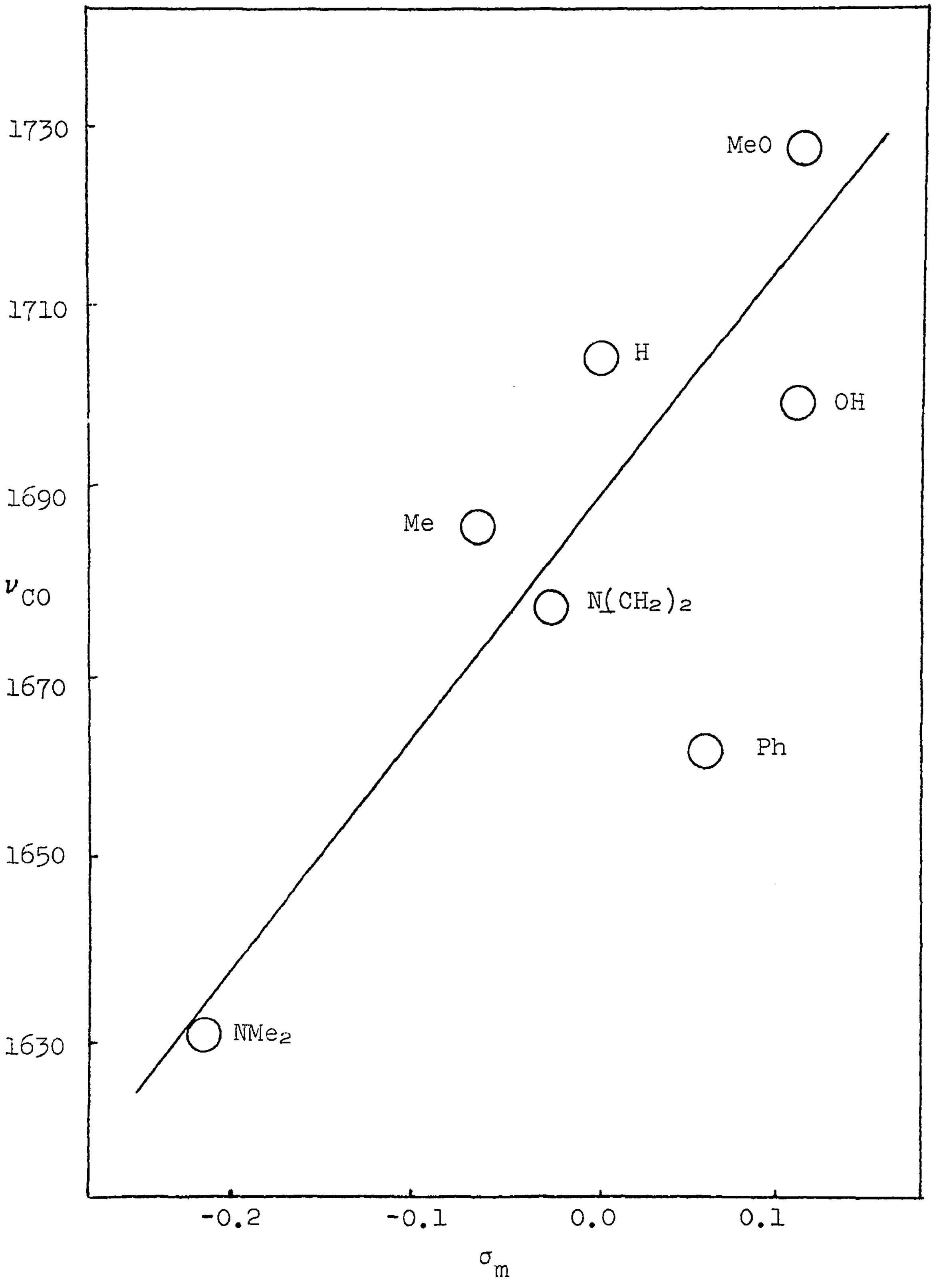
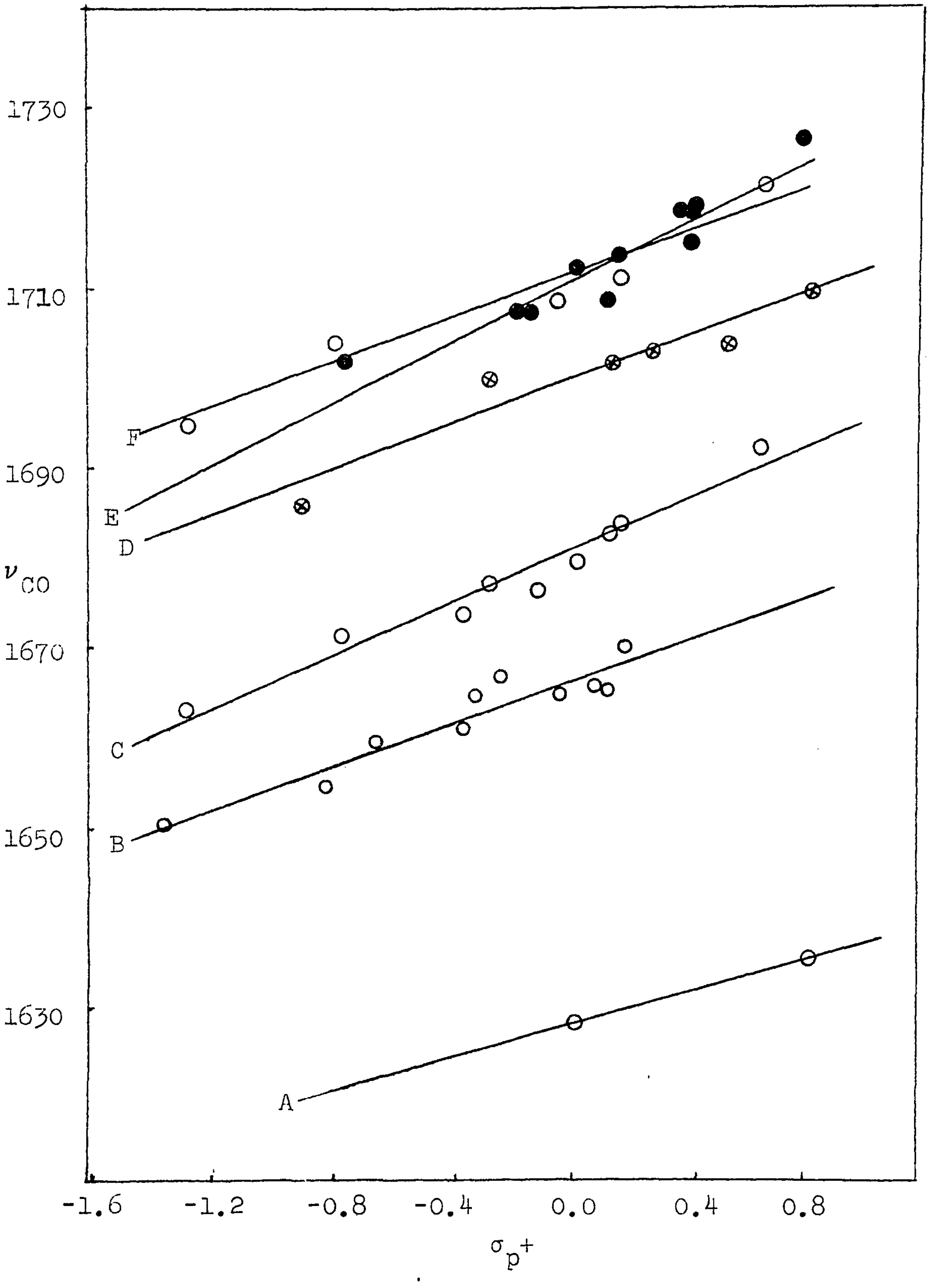

1730
1710
1690
1670
1650
1630
ν_{CO}
MeO
H
OH
Me
N(CH₂)₂
Ph
NMe₂
-0.2
-0.1
0.0
0.1
σ_m

Figure 9. The carbonyl stretching frequencies of benzoyl systems with carbonyl substituents NMe$_2$ (A), Ph (B), Me (C), H (D), OH (E, (●)), OEt (F, (○)), *vs*. σ_p^+ of the *p*-substituent


1730
1710
1690
1670
1650
1630
ν_{CO}
F
E
D
C
B
A
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
σ_p^+

frequency.

However, the determination of the σ^+ of the tricarbonylchromium substituent on benzoyl aziridine, 40, and on the 3-dimethylaminovinyl phenyl ketone, 45, (Table 12) systems is more indirect.

The σ_m parameter of the aziridine ring can be calculated from σ_I and σ_R (45) and is -0.03 (Equation 19).

$$\sigma_m = \sigma_I + \sigma_{R/3} \tag{19}$$

Also, the carbonyl frequency of benzoyl systems, PhCOR, is linearly correlated with σ_m (40) of the carbonyl substituent, R, and the observed frequency of the carbonyl in benzoyl aziridine, 39, corresponds to $\sigma_m = -0.06$ (Figure 8), in good agreement with the just calculated -0.03.

From Figure 8 and from the fact that the aziridine substituent gives about the same carbonyl frequency as does the methyl group (Table 12), we will assume that the carbonyl frequency of benzoyl aziridines will be as sensitive to the σ^+ of the ring substituent as is the carbonyl frequency of acetophenone (Figure 9). Therefore the σ^+ of the tricarbonylchromium substituent is 0.22.

The low 1554.8 cm^{-1} absorption for 3-dimethylaminovinyl phenyl ketone, 44, indicates that the dimethylaminovinyl group has a lower σ_m value than does the dimethylamino group, namely (Figure 8), $\sigma_m = -0.47$. We shall presume, therefore, that the carbonyl frequency of 3-dimethylaminovinyl phenyl ketone is a little less sensitive to σ^+ of ring substituents than it is for amides.. Complexation affects a 10.4 cm^{-1} increase in the carbonyl frequency (45); therefore, the tricarbonylchromium substituent is calculated to possess a σ^+ value of > +1.08.

We now have the apparent σ^+ of the tricarbonylchromium substituent in eight benzoyl systems. The apparent σ^+ parameter is a sum of inductive, σ^0, and release effects, $\sigma_A{}^+$, according to Equation 17. Table 13 shows the importance of the release mechanism in different benzoyl systems. The data is in accord with the idea that as the carbonyl substituent, R, becomes more electron releasing, the complexed arene becomes less so, compared to "normal" substituents.

In benzamide rotation

Amides have considerably high C-N bond order in the ground state. The free energy needed to break the C-N

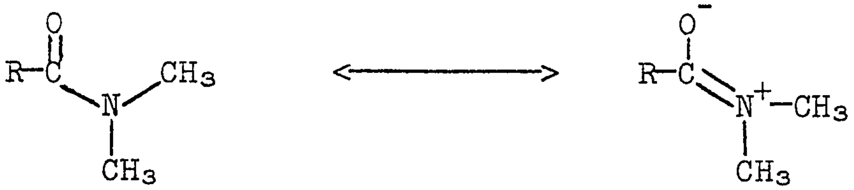
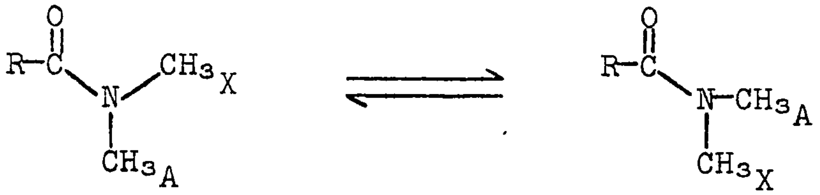


Table 13. The release sigma, σ_A^+, for the tricarbonylchromium group in benzoyl systems

Carbonyl substituent	σ^+	σ_A^+
H (36)	-0.474	-1.29
Ph (47)	0.10	-0.72
Me (33)	0.166	-0.65
$N(CH_2)_2$ (40)	0.22	-0.60
MeO (38)	0.22	-0.60
HO (49)	0.74	-0.08
NMe_2 (42)	0.83	0.01
$CH{=}CHNMe_2$ (45)	> 1.08	> 0.26

overlap by rotation of the dimethylamino group into a plane orthogonal to the acyl group is called the activation rotational free energy, Δ F*. The nmr shifts of the two N-methyl groups are different at low temperatures because the rate of interconversion of the rotamers is then



sufficiently slowed (46). At higher temperatures, the nmr "sees" only an "average" N-methyl group and the two N-CH_3 signals become one broad singlet. From the temperature and the half-height-width at the point of coalescence, which is that point when the two signals just become one flat-topped signal, one can calculate ΔF^* at the coalescence temperature, ΔF^*_{Tc} (see Experimental). Calculation of the activation free energy at a common temperature would be more appropriate (and more difficult, requiring a complete line shape treatment (47, 48, 49, 50, 51, 52)); however, the free energy temperature dependence corresponds to the activation entropy, Equation 20, and since the activation entropies for

$$\delta \Delta F^*/\delta T = \Delta S^* \qquad (20)$$

structurally similar amides are almost certainly equal, and are probably about zero, ranging from -5 to +10 entropy units in rotational phenomena (47, 48, 49, 50, 51, 52, 53, 54), such an adjustment is unnecessary.

The activation free energies for rotation for eleven *p*-substituted N,N-dimethylbenzamides were determined at their coalescent temperatures (Table 14). The plot of the free energy, ΔF^*_{Tc}, *vs.* σ^+ of the *p*-substituent (Figure 10) showed a slope corresponding to $\rho = -0.91$. The barrier of (N,N-dimethylbenzamide)tricarbonylchromium,

Table 14. The activation free energies for rotation of p-substituted N,N-dimethylbenzamides[a]

p-Substituent	T_c[b]	δ_{AX}[c,d]	ΔF^{*}_{Tc}[e,f]
H (41)	20.5	9.2	15.42[g]
Me	13.4	7.7	15.14
i-Pr	10.0	7.4	14.98
t-Bu	12.0	6.8	15.14
MeO	-4.4	5.3	14.38
F	12.0	7.9	15.06
Cl	15.5	8.7	15.20

---

[a] All amides were diluted to 0.22-0.23 M in chloroform that was freed from ethanol and distilled; the solutions were subjected to nmr study within 12 hours. When allowed to stand longer, this ethanol-free chloroform accumulated traces of acid and the barriers determined were then observed to be lower.

[b] The temperature at which the N-methyl absorptions just became a singlet, in degrees centigrade.

[c] The difference in chemical shifts of the N-methyl groups, as measured at the coalescence temperature (width at half height), in Hz.

[d] Estimated maximum error ± 2.0 Hz unless otherwise noted.

[e] The free energy of activation for rotation at the coalescence temperature, in kcal/mole.

[f] Calculated maximum error ± 0.30 kcal/mole.

[g] Rodgers and Woodbrey report a value of 15.3 kcal/mole in methylene bromide (46).

Table 14 (Cont.)

p-Substituent	T_c [b]	δ_{AX} [c,d]	$\Delta F^{*}_{T_c}$ [e,f]
Br	19.5	8.8	15.40
Ph	13.0	7.2	15.13
NH_2	-29.7	2.16[h]	13.43
NO_2 (43)	37.0	11.4	16.22
CN	33.7	11.2[i]	16.05
π-$Cr(CO)_3$ (42)	-20.5	9.5	13.20

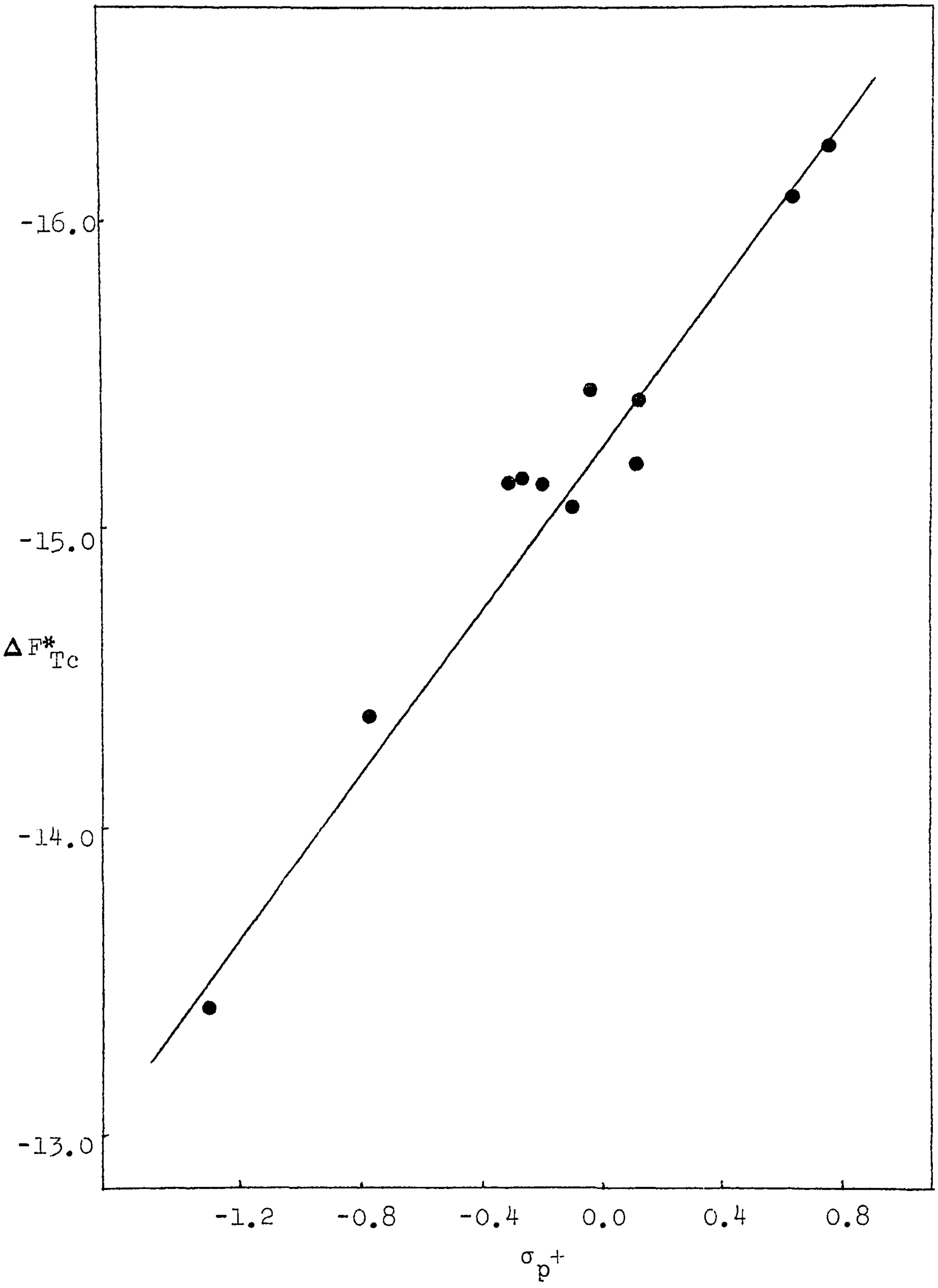
[h] Estimated maximum error ± 0.5 Hz.

[i] Estimated maximum error ± 3.0 Hz.

42, corresponds to a σ^+ value for the tricarbonylchromium substituent of -1.63 ± 0.15. Subtraction of the inductive parameter, σ^o, from this value gives the release parameter, σ_A+, -2.45 ± 0.15, effective in rotation (Equation 17). The ground state σ_A+ is 0.01 (Table 13). Therefore the σ_A+ effective <u>at</u> the transition state is -2.45 - 0.01 = -2.46. Table 13 shows that the σ_A+ value generally decreases (more releasing) as the intuitively estimated demand increases.

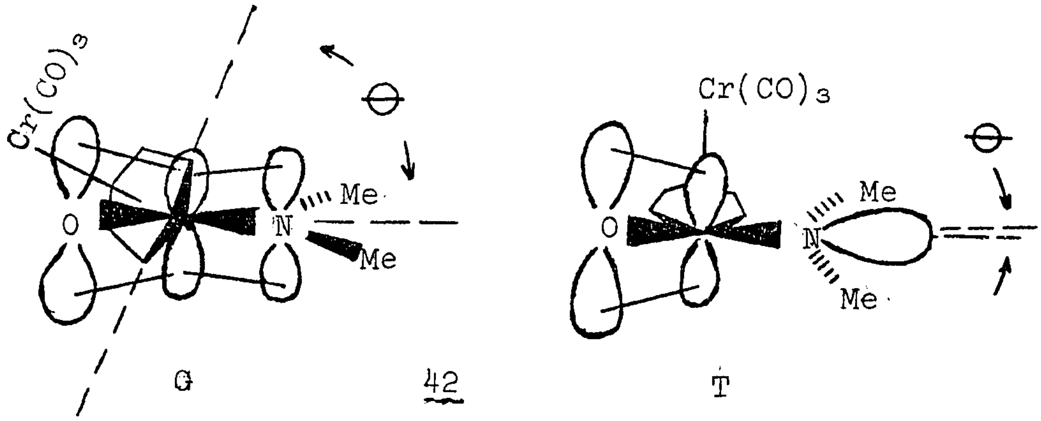
The σ_A+ value at the transition state, -2.46, is more negative than for benzaldehyde, -1.29, even though the

Figure 10. Free energy of activation for rotation of N,N-dimethylbenzamides *vs*. σ^+ of the *p*-substituent


-16.0
-15.0
-14.0
-13.0
ΔF^*_{Tc}
-1.2
-0.8
-0.4
0.0
0.4
0.8
σ_p^+

dimethylamino group is more electron releasing than a hydrogen. Moreover, the $\sigma_A{}^+$ value at N,N-dimethylbenzamide ground state is 0.01 so that the <u>change</u> in release during rotation, $\sigma_A{}^+$, is -2.45 units. This must reflect the relative geometries of ground and transition states.

The ground state of (N,N-dimethylbenzamide)tricarbonylchromium probably involves a large dihedral angle, θ, between the planes of the carbonyl and phenyl groups, 42G.



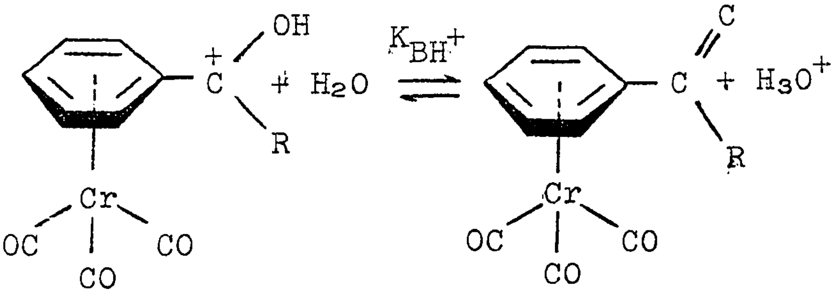
42

In this state the demand of the carbonyl upon the phenyl group (and the tricarbonylchromium group) is lessened by the ability of the dimethylamino group to respond to that demand. Indeed the metal release is one of the smallest for any of the benzoyl systems studied, $\sigma_A{}^+ = 0.01$. However, the barrier to rotation is best broken by allowing the phenyl ring to release electrons into the carbonyl, reducing the dihedral angle θ to a near zero value, so that the C-N bond order can become small. Such a transition state formulation (42T) turns the dimethylamino group into an electron demanding group, compared to hydrogen, so that the response of the tricarbonylchromium ($\sigma_A^+ = -2.45$) is more than that in the benzaldehyde system ($\sigma_A^+ = -1.29$).

In α-hydroxybenzyl cations

Formation When ethanol solutions of tricarbonylchromium complexes of benzaldehyde, acetophenone, benzoic acid, N,N-dimethylbenzamide, and benzophenone are injected into highly concentrated (87-97%) sulfuric acid, a new spectral absorption pattern is observed (Table 15).

When the intensely colored solutions of these complexes in highly concentrated sulfuric acid are poured upon ice, the starting complexed benzoyl compounds can be recovered. We interpret the facts to mean that, with the possible exclusion of the amide (which may suffer N-protonation (55)), the complexes, 50, undergo reversible O-protonation to establish an equilibrium between the benzoyl system and α-hydroxybenzyl cation, 51.



(21)

51 50

Table 15. The ultraviolet-visible spectra of (benzoyl)tricarbonylchromium systems in ethanol, water, and sulfuric acid[a]

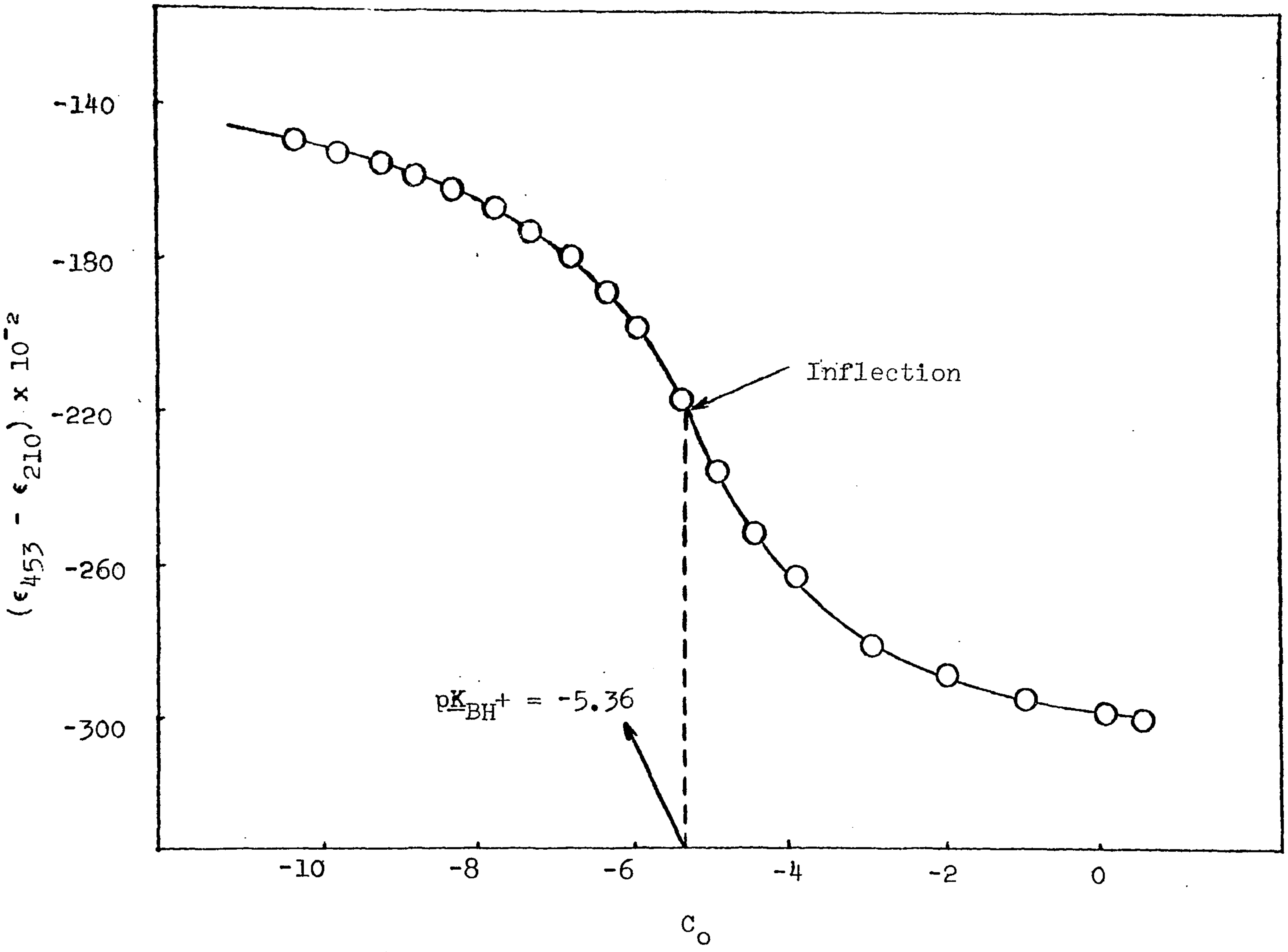
Compound	95% ethanol	Water	87-94% sulfuric acid
π-(PhCHO)Cr(CO)$_3$ (36)	2135(28400) 3200(9620) 2620(6110) 4180(2380)	2130(30400) 2670(5940) 3200(8830) 4230(3400)	2100(21600) 2950(14700) 3330(4650) 4530(3920)
π-(PhCOMe)Cr(CO)$_3$ (33)	2100(31400) 2660(6100) 3230(9660) 4140(2920)	2100(31530) 2660(6110) 3210(8840) 4170(3180)	1970(20500) 2140(20600) 2960(10380) 3290(5060) 4850(5310)
π-(PhCOPh)Cr(CO)$_3$ (47)	2000(36900) 2530(15000) 3260(8860) 4340(3610)	3210(8300)[b] 4390(3920)[b]	2930(13850) 3470(16650) 5250(5790)
π-(PhCO$_2$H)Cr(CO)$_3$ (49)		2180(23100) 2600(5460) 3180(8890) 3970(2060)	2090(24600)[c] 2600(9280) 3160(4250) 4530(4090)
π-(PhCONMe$_2$)Cr(CO)$_3$ (42)	2180(27100) 2540(8990) 3200(10400) 4000(1415)	2160(28700) 2530(8500) 3190(9710) 3960(1450)	2040(22000) 3250(5600) 3390(5300) 4280(2450)

[a] All absorptions in Angstroms; molar extinction coefficients are parenthesized.

[b] Due to limited solubility in water, 5 cm cells were necessarily employed; they were not balanced well for the 2000-2600 Angstrom range.

[c] The molar extinction coefficient increased with time; this absorption could have arisen from the formation of the free cation.

Figure 11. The difference of the molar extinction coefficients at 4530 Å and 2100 Å for (benzaldehyde)tricarbonylchromium vs. H_0 of the sulfuric acid-water solvent


-140
-180
-220
-260
-300
$(\epsilon_{453} - \epsilon_{210}) \times 10^{-2}$
-10
-8
-6
-4
-2
0
C_o
Inflection
$p\underline{K}_{BH^+} = -5.36$

The basicities of ring-substituted benzaldehydes (56), acetophenones (57), benzoic acids (43), benzamides (55), and benzophenones (58) have been quantitatively evaluated by the Hammett acidity (H_o) method (59). Thus for Equation 21,

$$p\underline{K}_{BH^+} = H_o + \log\ ([\underset{\sim}{51}]/[\underset{\sim}{50}]) \qquad (22)$$

Values of H_o for various mixtures of sulfuric acid and water are tabulated (60), and the term $[\underset{\sim}{51}]/[\underset{\sim}{50}]$ can be determined spectroscopically.

The $p\underline{K}_{BH^+}$ calculations for free and complexed acetophenone, benzaldehyde, benzophenone, benzoic acid, and N,N-dimethylbenzamide depend upon the plot of $\epsilon_{\lambda_1} - \epsilon_{\lambda_2}$ against H_o, where λ_1 and λ_2 are bands whose molar extenction coefficients, ϵ, increase and decrease, respectively, with increasing acid concentration. The H_o value at which inflection occurs is the $p\underline{K}_{BH^+}$ value (33). A typical plot, that for complexed benzaldehyde, is Figure 11.

The $p\underline{K}_{BH^+}$ values of all compounds investigated and the effect of the tricarbonylchromium group, $\Delta\, p\underline{K}_{BH^+}$, are tabulated below (Table 16).

Variable electron release   The effect of the tricarbonylchromium substituent upon $p\underline{K}_{BH^+}$ is related to the ability of the carbonyl substituent to overlap with

Table 16. The increase of the pK_{BH^+} values of α-hydroxylbenzyl cations upon complexation[a]

Cation	pK_{BH^+}	Reference	ΔpK_{BH^+} [b]
$PhCHOH^+$ (52)	-7.11 -7.10	(56)	
π-$(PhCHOH)Cr(CO)_3^+$ (53)	-5.46		+1.65
$PhC(OH)Me^+$ (54)	-5.91 -6.15	(57)	
π-$(PhC(OH)Me)Cr(CO)_3^+$ (55)	-5.96		-0.05
$PhC(OH)Ph^+$ (56)	-6.13 -6.18	(58)	
π-$(PhC(OH)Ph)Cr(CO)_3^+$ (57)	-5.68		+0.45
$PhC(OH)_2^+$ (58)	-7.20 -7.26	(43)	
π-$(PhC(OH)_2)Cr(CO)_3^+$ (59)	-8.02		-0.82
$PhC(OH)NMe_2^+$ (60)	-1.37 -1.62	(55)	
π-$(PhC(OH)NMe_2)Cr(CO)_3^+$ (61)	-3.10		-1.73

[a] The estimated maximum error in pK_{BH^+} values for the uncomplexed systems is ± 0.30 units; for the complexed systems, ± 0.50 units.

[b] Calculated using our values for the free and complexed system.

the carbonyl: the σ_m parameter (Figure 12) is inadequate while σ_p (Figure 13) and σ_p^+ (Figure 14) show fair correlations with $\Delta p\underline{K}_{BH^+}$.

Clearly, then, the effect exerted by the tricarbonylchromium group on the α-hydroxybenzyl cation acidities depends upon how the carbonyl is substituted, just as was the case with the carbonyl stretching frequencies of their conjugate bases (Table 13). In particular, the effect of the tricarbonylchromium substituent appears to be related, to a large extent, to the ability of the benzylic substituent to donate electrons to the vacant orbital by resonance.

The $p\underline{K}_{BH^+}$ values for benzaldehyde (56), acetophenone (57), benzophenone (59), benzoic acid (43), and to a lesser degree, N,N-dimethylbenzamide (55) are linearly related to σ^+ of the ring substituents within a given system. For benzamide, σ gives a slightly better fit than σ^+ (55). Assuming that ρ for N,N-dimethylbenzamides is the same as that for benzamides, we can then accumulate the σ^+ and the σ_A^+ values (calculated by subtracting σ^o from σ^+ (see Equation 17)) for the tricarbonylchromium substituent in those systems (Table 17).

The fact that the nature of the interaction of the tricarbonylchromium group with the carbonyl in the benzoyl systems (Table 13), on the one hand, and with the carbonium ion in the α-hydroxybenzyl cation, on the other, is

Figure 12. The increase of the $p\underline{K}_{BH^+}$ values of α-hydroxybenzyl cations upon complexation *vs*. σ_m of the α-substituent

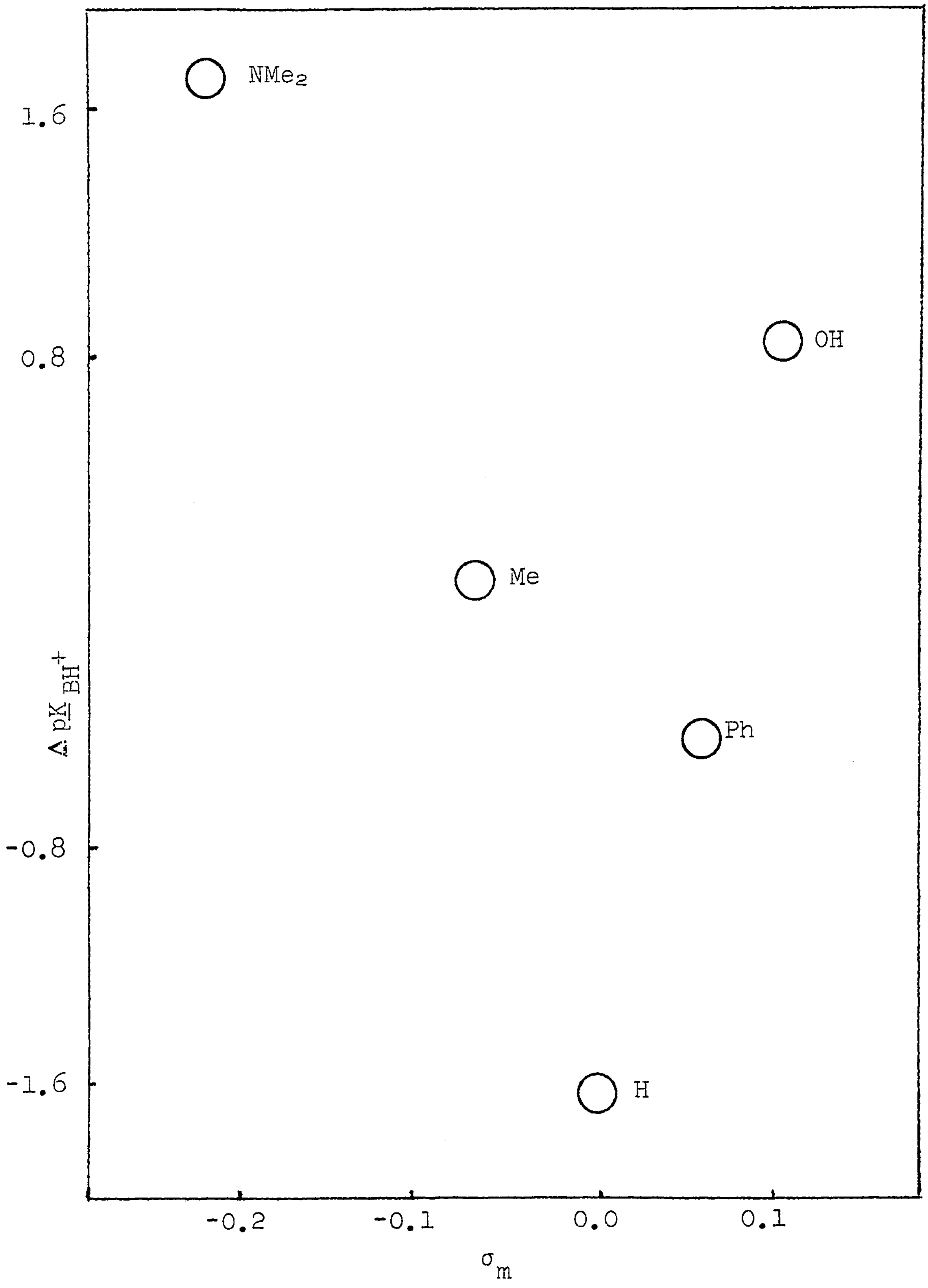

NMe₂
OH
Me
Ph
H
1.6
0.8
-0.8
-1.6
$\Delta\,p\underline{K}_{BH^+}$
-0.2
-0.1
0.0
0.1
σ_m

Figure 13. The increase of the $\underline{pK}_{BH^+}$ values of α-hydroxybenzyl cations upon complexation *vs*. σ_p of the α-substituent

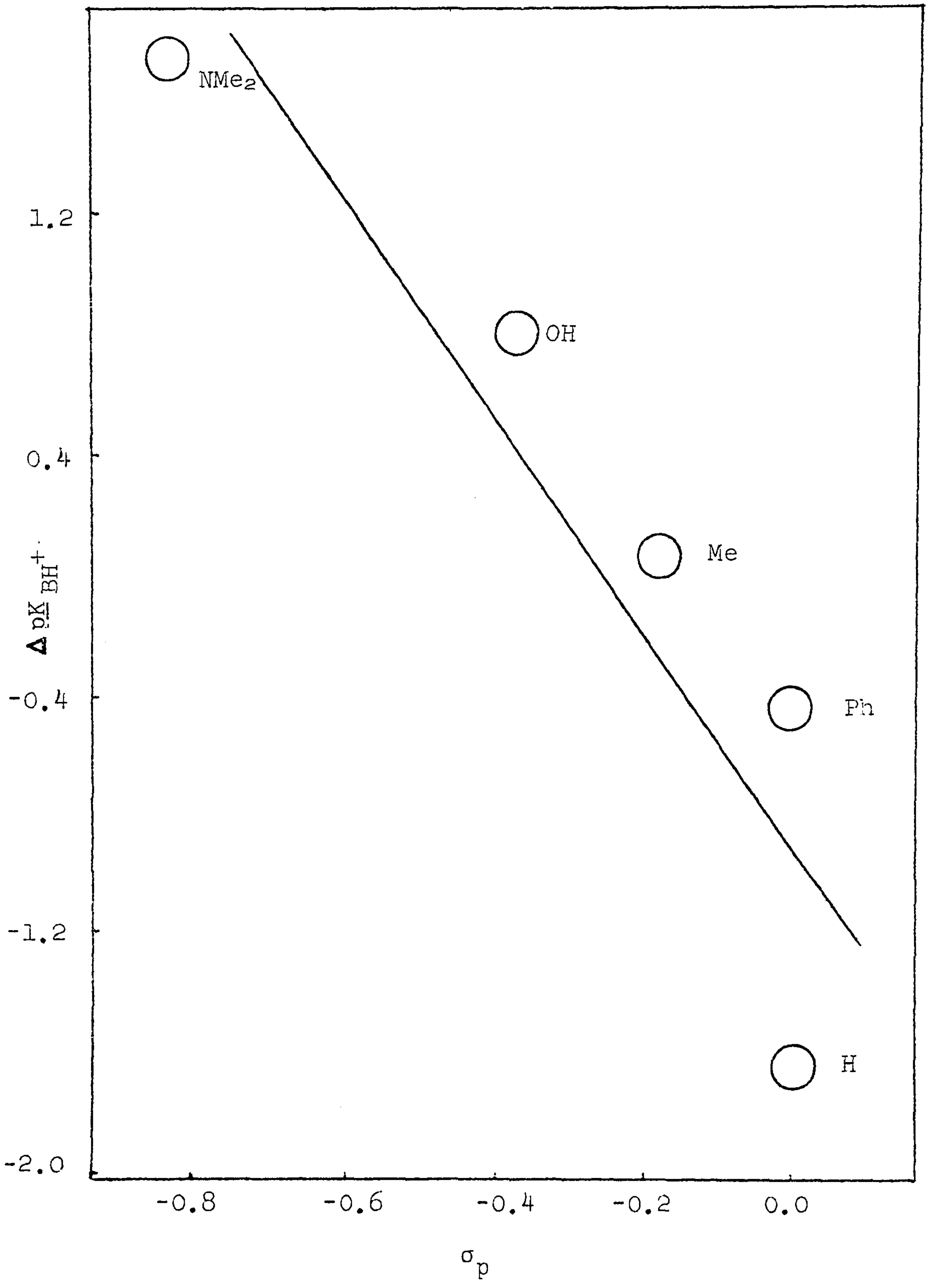

NMe₂
OH
Me
Ph
H
1.2
0.4
-0.4
-1.2
-2.0
-0.8
-0.6
-0.4
-0.2
0.0
Δ pK BH+
σp

Figure 14. The increase of the $p\underline{K}_{BH^+}$ values of α-hydroxybenzyl cations upon complexation *vs*. σ_p^+ of the α-substituent

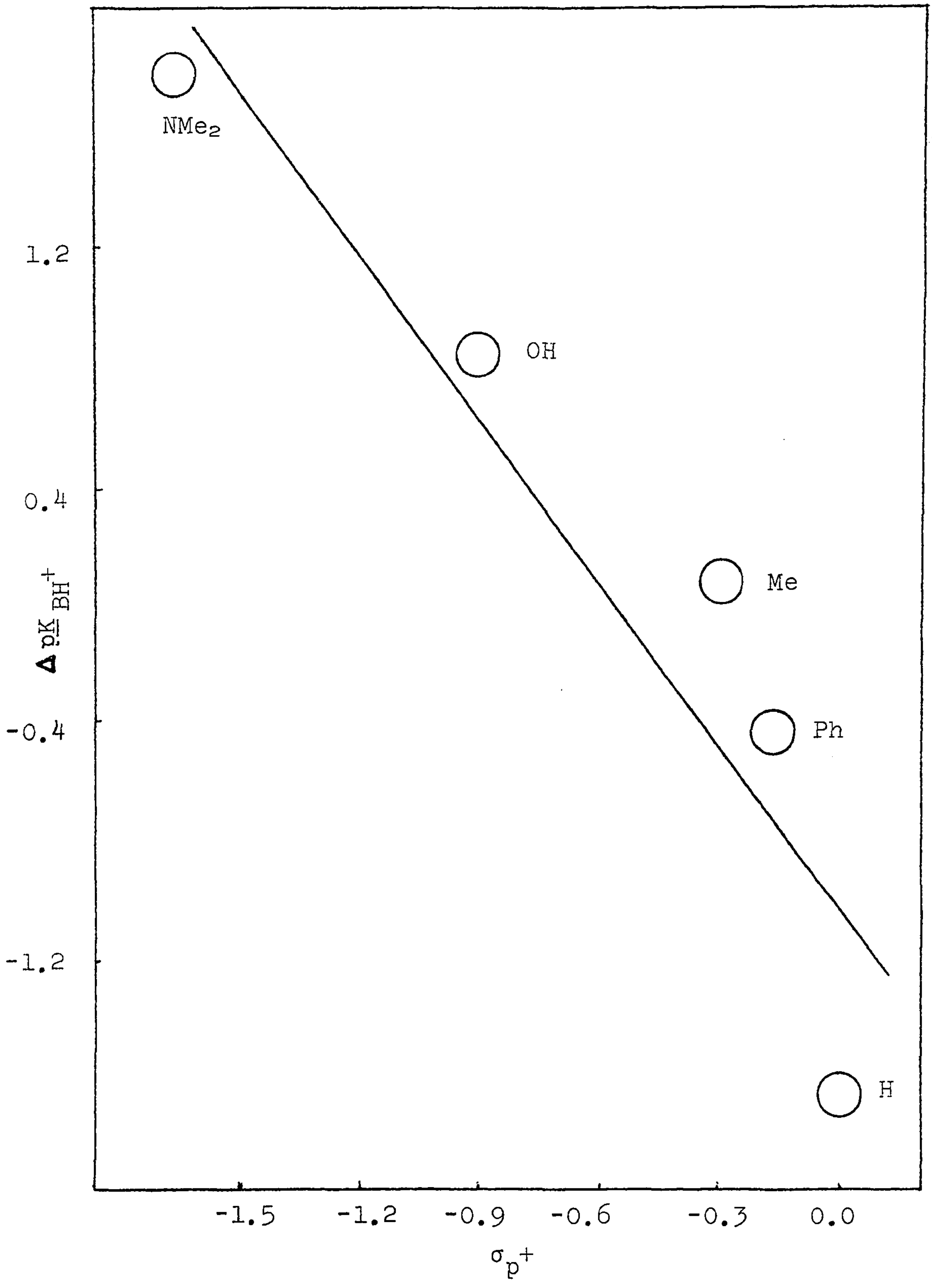

NMe₂
OH
Me
Ph
H
1.2
0.4
-0.4
-1.2
Δ pK_BH+
-1.5
-1.2
-0.9
-0.6
-0.3
0.0
σp+

Table 17. The σ^+ and σ_A^+ values for the tricarbonylchromium group in α-substituted, α-hydroxybenzyl cations

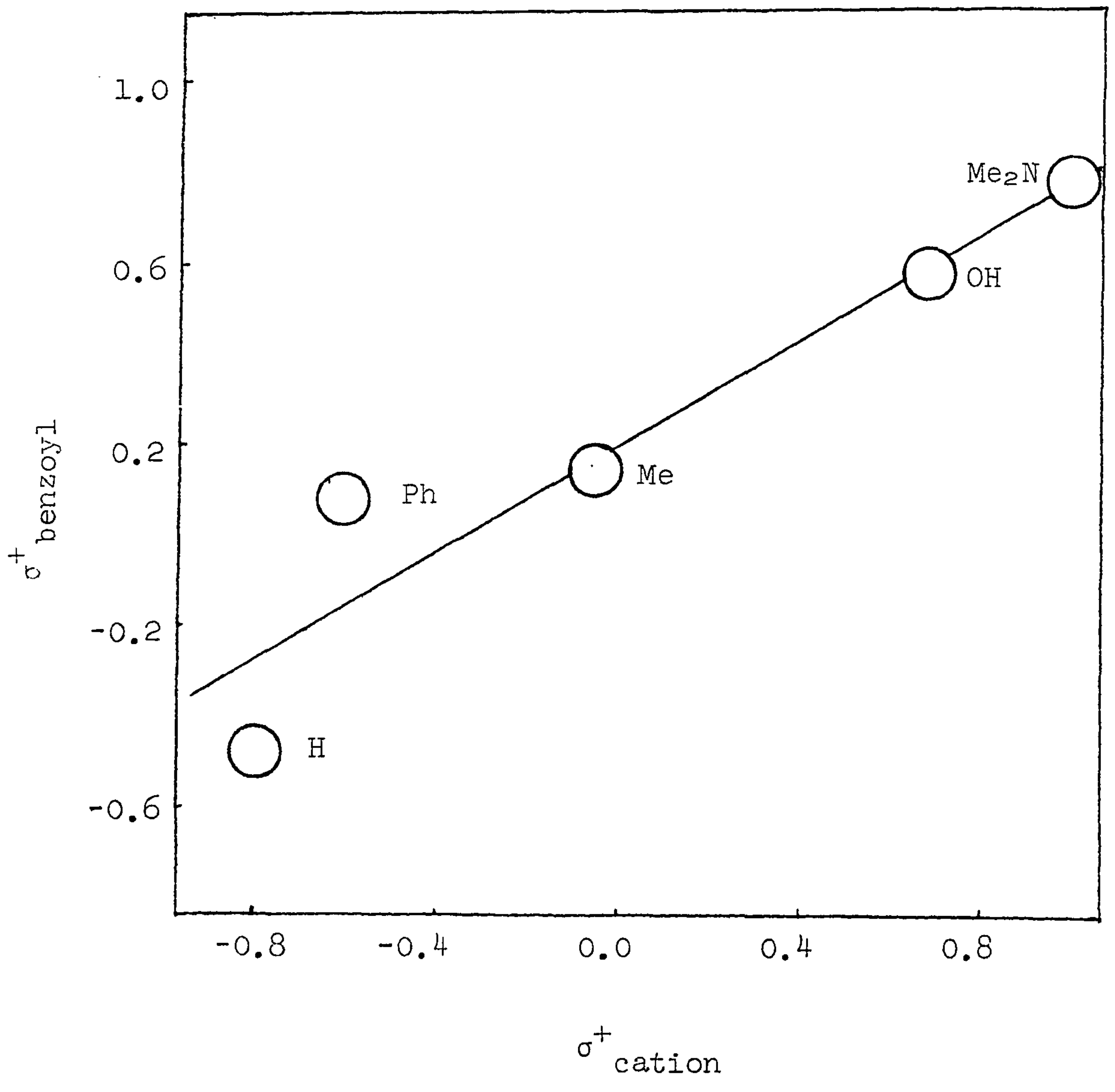
α-Substituted	σ^+	σ_A^+
H (53)	-0.80	-1.62
Me (55)	-0.066	-0.89
Ph (57)	-0.6	-1.4
HO (59)	+0.65	-0.17
NMe_2 (61)	+0.95	+0.13

similar, is suggested by parallel behavior of the σ^+ (or σ_A^+) values in the respective systems (Figure 15).

In diphenylmethyl cations

Formation We have determined the stability of a pair of complexed diphenylmethyl cations by the procedure used for the complexed benzyl cations. The attempt to determine the spectra of these cations was made difficult by the tendency of the complexed diphenylmethyl cations to rapidly decompose to the free cations at high sulfuric acid concentration. Consequently, only 18% recovery of (diphenylmethanol)tricarbonylchromium could be established.

Figure 15. The σ^+ of the tricarbonylchromium substituent in the benzoyl systems vs. the σ^+ of the tricarbonylchromium substituent in the α-hydroxybenzyl cation systems


1.0
0.6
0.2
-0.2
-0.6
$\sigma^+_{benzoyl}$
Me₂N
OH
Me
Ph
H
-0.8
-0.4
0.0
0.4
0.8
σ^+_{cation}

Shown below is the plot of ϵ, the molar extinction coefficient at 4420 Å, the λ_{max} for (diphenylmethyl)tricarbonylchromium cation, 62, as a function of the acidity, expressed in C_o units (Figure 16). The inflection at the higher (less negative) C_o value corresponds to the $pK_R{}^+$ of the complexed cation, 29, whose extinction coefficient at 4420 Å was much larger than for the complexed cation (Table 18).

Table 18. The visible spectra and pK_R+ values of diphenylmethyl cations and their tricarbonylchromium complexes

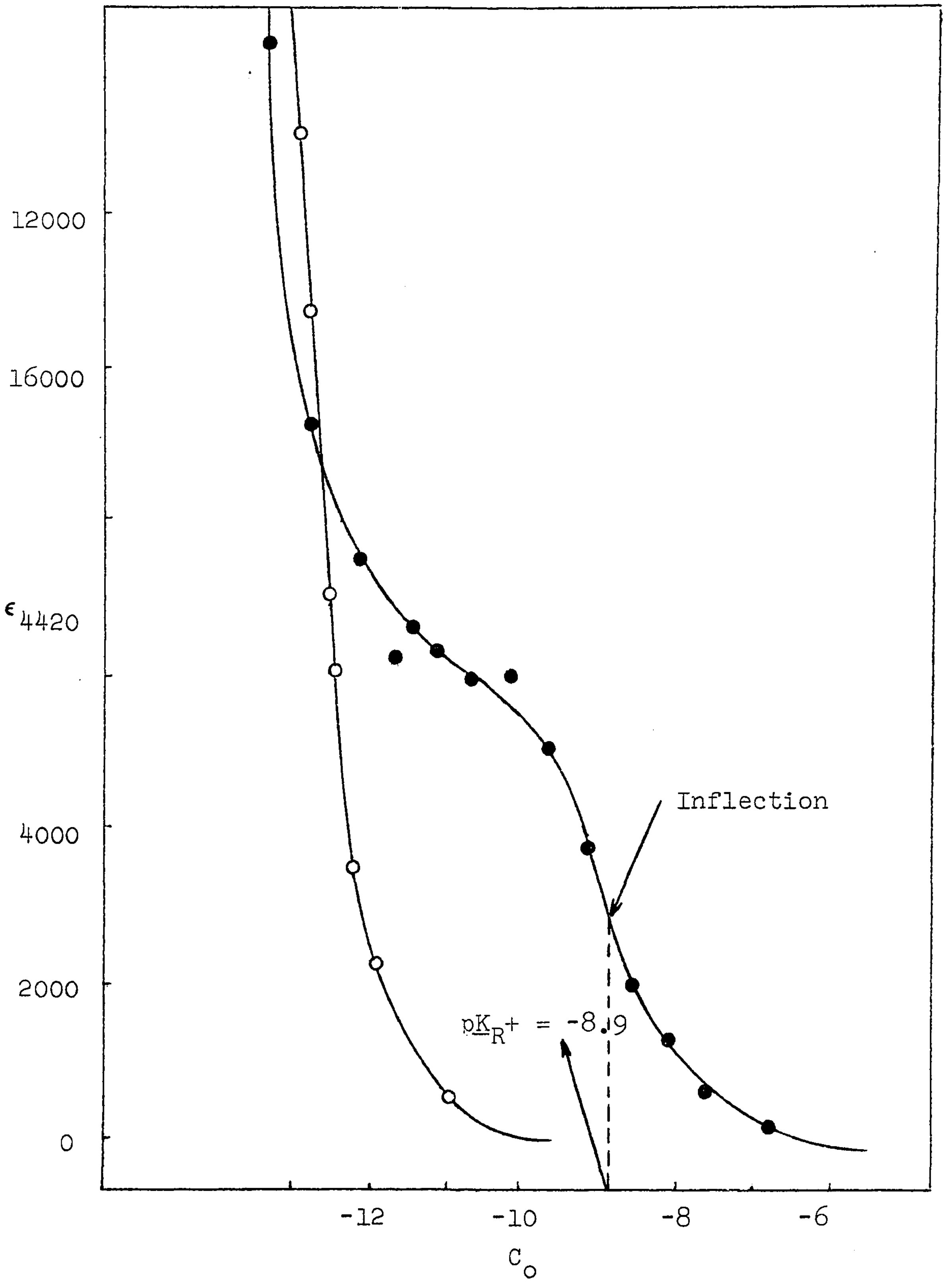
Cation	Visible absorption[a]	pK_R+
Ph_2CH^+ (29)	4420(61000)	-13.4 -13.3[b]
π-$(Ph_2CH)Cr(CO)_3{}^+$ (62)	4420(6000)	- 8.9
p-MeOPhCHPh$^+$ (63)	4660(33100)[b]	- 7.9[c]
π-(*p*-MeOPhCHPh)$Cr(CO)_3{}^+$ (64)	5610(12000)	- 7.1
p,p'-$(MeOPh)_2CH^+$ (65)		- 5.7[c]

[a] Given in Angstroms; the molar extinction coefficients are parenthesized.

[b] Reference 32.

[c] N. C. Deno and Alan Schriesheim, J. Am. Chem. Soc., 77, 3051 (1954).

Figure 16. The molar extinction coefficient for free and complexed diphenylmethyl cation at 4420 Å *vs.* C_o for the sulfuric acid-water solvent


12000
16000
ε 4420
4000
2000
0
-12
-10
-8
-6
C_o
Inflection
p$\underline{K}_R$+ = -8.9

Variable electron release This particular series of cations would be, if it were more extensive, able to resolve just what the tricarbonylchromium moiety "listens" to before it decides its response to the electron demand by the carbonium ion center. The α-hydroxybenzylic carbonium work revealed that α-substituent electron donation by resonance is important (Figures 13 and 14), but steric differences between the various α-substituents makes tenuous any firm conclusions. A series of p-substituted diphenylmethyl cations, however, would have identical steric bulks at their cationic sites. Unfortunately, the appropriate complexes are difficultly obtainable, and only the pK_{R^+} for (p-methoxydiphenylmethyl)tricarbonylchromium cation, 64, was obtained (Table 18).

From the literature pK_{R^+} values for p-substituted diphenylmethyl cations (32) and the σ^+ values for the substituent, one can calculate (Figure 17) that the σ^+ value for the tricarbonylchromium group in the complexed diphenylmethyl cation is -0.88.

From the pK_{R^+} values for p,p'-dimethoxydiphenylmethyl cation, 65, and p-methoxydiphenylmethyl cation, 63, one can construct a two-point free energy relationship (Figure 18). The σ^+ of the tricarbonylchromium group, from the pK_{R^+} of (p-methoxydiphenylmethyl)tricarbonylchromium cation, 64, is -0.26. The $\sigma_A{}^+$ values are calculated by subtracting σ° from the σ^{+} values (see Equation 17) and are given in Table 19.

Table 19. The σ^{+} parameters of the tricarbonylchromium group in (benzyl)tricarbonylchromium cations

Cation	σ^{+}	$\sigma_{A}{}^{+}$
π-$(PhCH_2)Cr(CO)_3{}^{+}$ (16)	-1.42[a]	-2.24
π-$(Ph_2CH)Cr(CO)_3{}^{+}$ (62)	-0.88[b]	-1.70
π-(p-MeOPhCHPh)$Cr(CO)_3{}^{+}$ (64)	-0.26[b]	-1.08

[a] From solvolysis of (benzyl chloride)tricarbonylchromium, 2.

[b] From $pK_{R}{}^{+}$ values.

The summarized results for the following various electron-deficient complexed systems (Table 20) leave no doubt that tricarbonylchromium shows an extraordinary ability to vary its electron release (measured by its $\sigma_{A}{}^{+}$ value) to a deficient center according to the degree of electron demand.

Table 20. The σ_A+ values for the tricarbonylchromium group in various electron deficient systems

System	σ_A+
$PhCONMe_2$ (42)	-2.45[a]
$PhCH_2^+$ (16)	-2.36[b]
Ph_2CH^+ (62)	-1.70[c]
$PhCH(OH)^+$ (53)	-1.62[d]
PhCHO (36)	-1.29[e]
p-$MeOPhCHPh^+$ (64)	-1.08[c]
$PhC(OH)Ph^+$ (57)	-0.72[d]
$PhC(OH)_2^+$ (59)	-0.17[d]
$PhCONMe_2$ (42)	0.01[e,f]
$PhC(OH)NMe_2^+$ (61)	0.13[d]
$PhCOCH=CHNMe_2$ (45)	> 0.26[e]

[a] At the rotational transition state.

[b] From solvolysis of (benzyl chloride)tricarbonylchromium (2).

[c] From pK_R+ value.

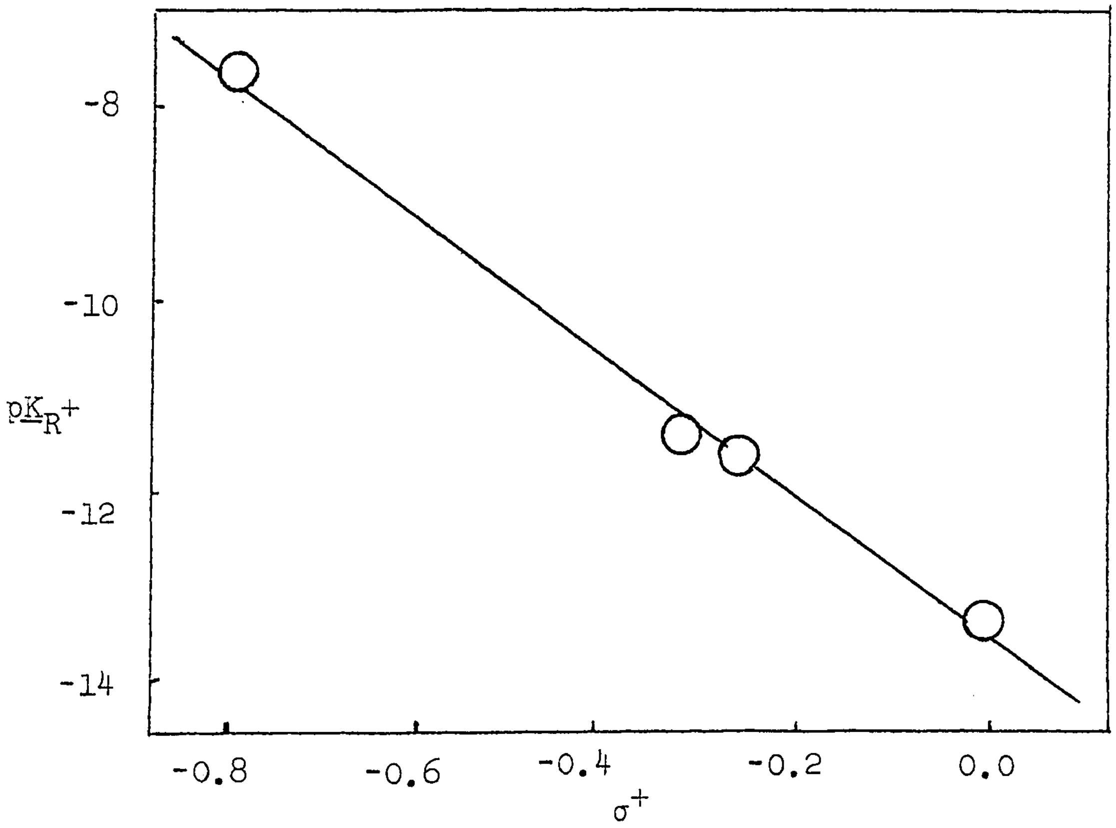
[d] From $pK_{BH}+$ value.

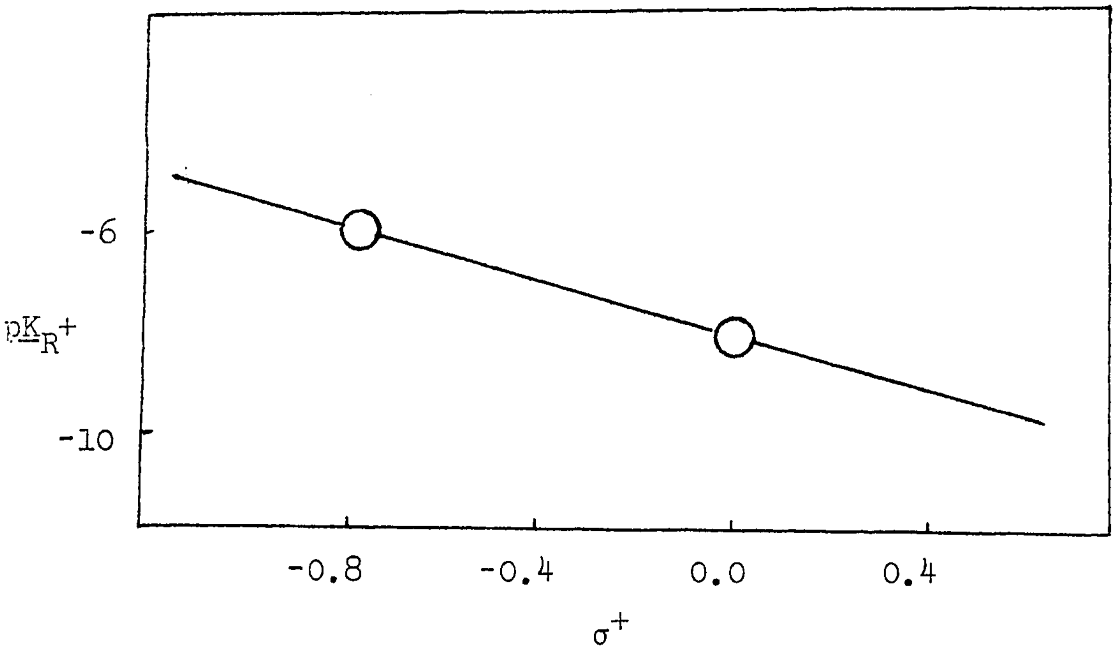
[e] From ir frequencies.

[f] At the rotational ground state.

Figure 17. The pK_{R^+} values for diphenylmethyl cations *vs.* the σ^+ of the *p*-substituent

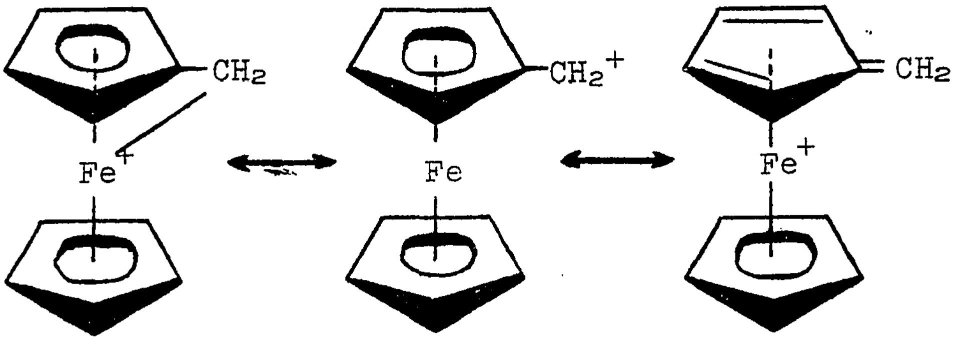
Figure 18. The pK_{R^+} values for *p*-methoxydiphenylmethyl cations *vs.* the σ^+ of the *p*'-substituent


-8
-10
-12
-14
pK_R+
-0.8
-0.6
-0.4
-0.2
0.0
σ+


-6
-10
pK_R+
-0.8
-0.4
0.0
0.4
σ+

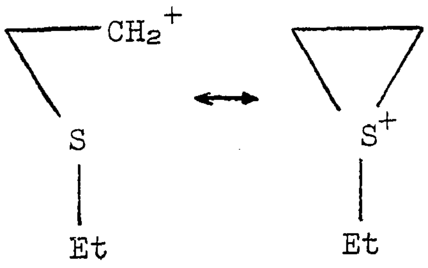
Candidate Mechanisms: "σ-d Participation" and "σ-π Hyperconjugation"

The ferrocenylmethyl cation is very stable, as measured both by direct means (pK_{R^+}) (16), by the rates of solvolyses of the appropriate acetates (15, 17, 18) and chlorides (19), and by the ease of protonation of vinylferrocene (61-62). Two mechanisms have been considered by ferrocene chemists: "σ-d participation," sponsored by Hill and Richards (15) and Cais _et al._ (20), and "σ-π hyperconjugation," favored by Traylor and Ware (19). Both schemes take advantage of the metal's willingness to become positively charged.



66 7 67

The "σ-d" model, 66, resembles the depiction of a "neighboring group" interaction, the conversion of a sigma non-bonding electron pair to a bonding sigma pair, as in the stabilization (19) of β-ethylthioethyl cation, 68. The "σ-π" model, 67, resembles a hyperconjugative interaction, as in the stabilization of a carbonium ion by a β-methyl group, 69.



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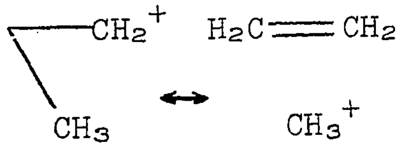
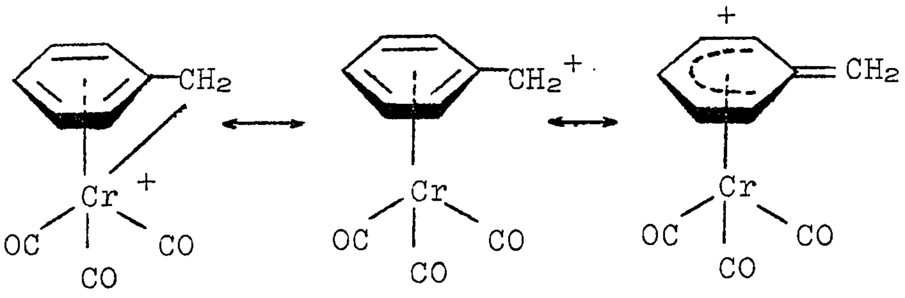


69

The present status of the ferrocenyl cation problem has been discussed by Feinberg and Rosenblum (22).

Justification for the adaptation of models 66 and 67 to the tricarbonylchromium system resides in the fact that this system and the ferrocene system are isoelectronic. The result is two pictures for the complexed cation, representing, again, the "σ-d" and "σ-π hyperconjugative" models 70 and 71.

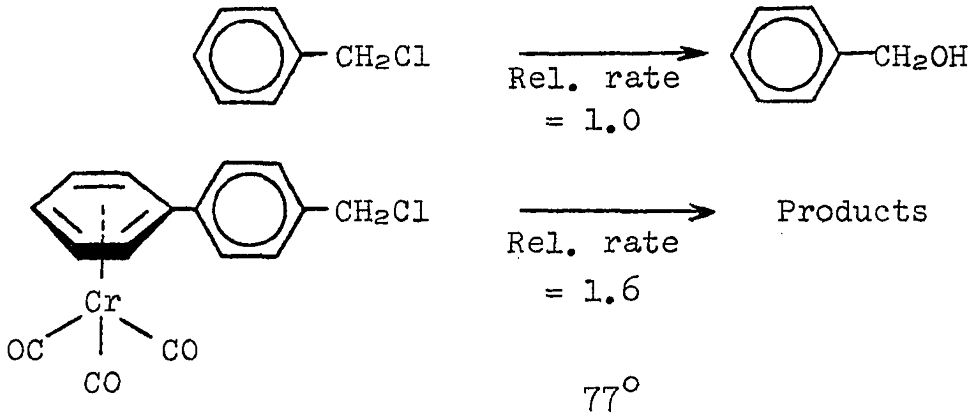


70 16 71

"Neighboring group" vs. "hyperconjugative" group criteria tested

According to Traylor and Ware (19), the relative ability to assist cation formation para and α to the reaction site is a basis for whether the "σ-d" or "σ-π" mechanism is operative. So that if the (phenyl)tricarbonylchromium group can assist solvolysis para to a cation as well as it does α, then it is a "hyperconjugative" group, implying model 71 is valid; if it cannot, then it is a "neighboring group," implying model 70 is operative.

We attempted to obtain some evidence for the nature of the group, in this regard, by solvolyzing p-((phenyl)tricarbonylchromium)benzyl chloride, 72. However, oxidation of



(23)

(24)

77°

72 80% aqueous acetone

the metal by the solvent makes tenuous any wanton embrace of the solvolysis data; anyway, the only partially S_N1 nature of the solvolysis would not permit a σ^+ calculation for the *para* group. Since solvolysis of α-methylbenzyl halide systems are negligibly S_N2, these systems would be more enlightening as to whether *p*-(phenyl)tricarbonylchromium is a "neighboring group" or a "hyperconjugative" group.

The "σ-d" model, **70**, implies movement toward the benzylic carbon; the "σ-π" model, **71**, away from the benzylic carbon. Substitution of bulky groups *para* to the cation might affect the movement of the metal so as to stabilize, or destabilize, the complexed cation.

Consequently the stabilities of selectively substituted (benzyl)tricarbonylchromium cations were compared to those values predicted (Table 21) on the basis of the free energy

Table 21. The pK_{R^+} values of ring-substituted tricarbonylchromium benzyl cations

Cation	pK_{R^+}, predicted[a]	pK_{R^+}, found[b]
$\pi\text{-}(\underline{p}\text{-}(\underline{t}\text{-}C_4H_9)C_6H_4CH_2)Cr(CO)_3^+$ (73)	-10.8	-11.9[c]
$\pi\text{-}(3,5\text{-}(\underline{t}\text{-}C_4H_9)_2C_6H_3CH_2)Cr(CO)_3^+$ (74)	-10.8	-10.6[d]
$\pi\text{-}(3,5\text{-}(CH_3)_2C_6H_3CH_2)Cr(CO)_3^+$ (75)	-11.5	-11.3[e]
$\pi\text{-}(\underline{p}\text{-}CH_3C_6H_4CH_2)Cr(CO)_3^+$ (22)		-11.0[f]
$\pi\text{-}(C_6H_5CH_2)Cr(CO)_3^+$ (16)		-11.8[f]

[a] From Figure 2; σ for the di-*meta*-substituents is 2 x σ_m.

[b] Estimated maximum error ±0.3 pK_{R^+} units.

[c] Visible absorption λ_{max} 5230 Å (250).

[d] Visible absorption λ_{max} 5250 Å (350).

[e] Visible absorption λ_{max} 5290 Å (350).

[f] From Table 8.

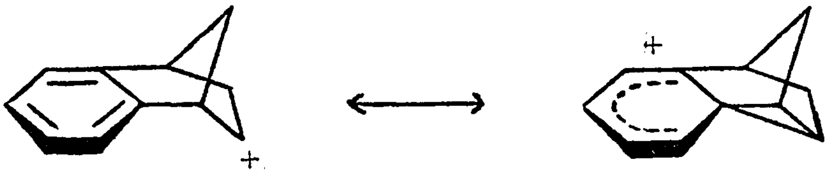
relationship between pK_{R^+} and σ (Figure 2).

From the cation data, there is barely the suggestion that two *m*-*t*-butyl groups aid release into the electron deficient center, whereas the *p*-*t*-butyl groups hinder release. Nevertheless, the attempt to distinguish between the two modes of stabilizing a benzyl carbonium on the basis of hindering or assisting the alledged tricarbonylchromium movement is not at all convincing in view of the quite small effects.

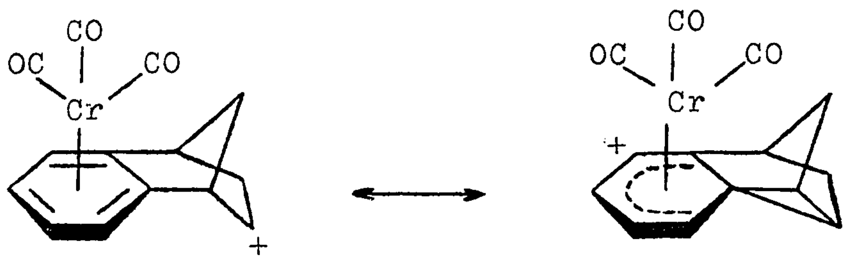
Establishment of Mechanism

The homo-benzylic cation

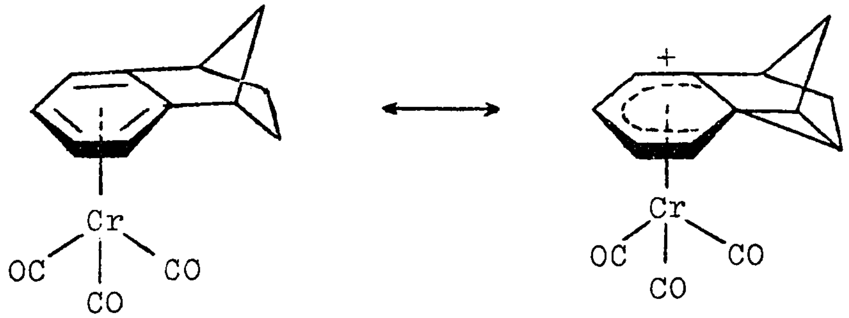
The benzylic cation appears to retain a good deal of its stability if a methyne is placed between the cation and the phenyl ring, as long as rigidity is maintained, as in a bicyclic system. Such an ion, 76, is "homo-benzylic," and has been postulated to be formed in the solvolysis of benzonorbornen-2-yl bromobenzenesulfonates (63, 64). To the extent that the ion involves the same kind of metal interaction as exists in the benzyl cation, we are given an excellent means of differentiating between the "σ-d" and "σ-π" mechanisms. If the "σ-π" structure is involved, then anti-, 77, or syn-, 78, tricarbonylchromium should stabilize the 2-cation equally well. If the "σ-d" structure



76

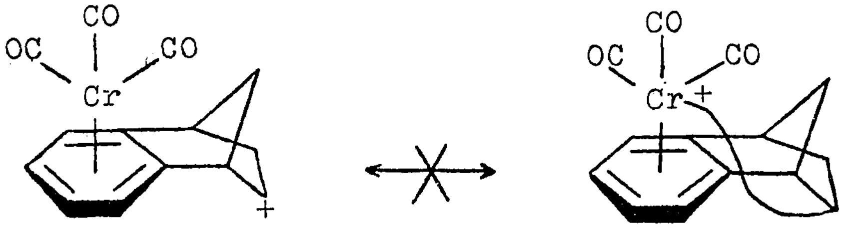


77

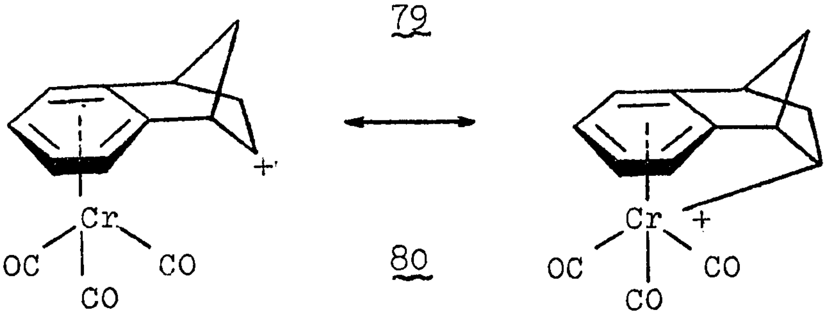


78

is involved, then the anti-(tricarbonylchromium) will be unable to assist in stabilizing the 2-cation, 79; the



79



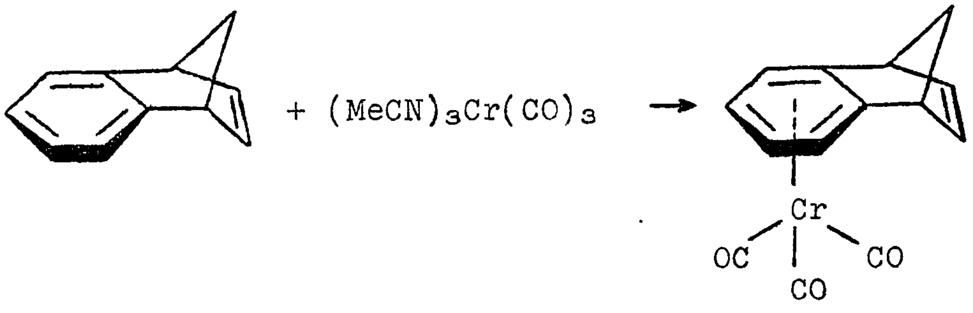
80

syn-(tricarbonylchromium) will, however, be confronted with no physical obstruction to the bonding of its nonbonding d electrons to the 2-carbon, 80.

A comparison of the solvolytic rates of various (benzonorbornen-2-yl bromobenzenesulfonate)tricarbonylchromiums should be unequivocable in determining which mechanism is operative.

Synthesis of (benzonorbornen-2-yl bromobenzenesulfonate)tricarbonylchromiums

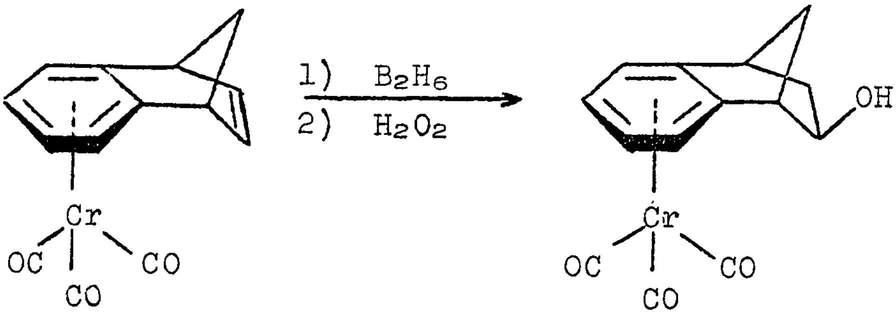
Syn-(benzonorbornen-2(exo)-yl bromobenzenesulfonate)tricarbonylchromium A mixture of benzonorbornadiene, 81, and (triacetonitrile)tricarbonylchromium, 82, was refluxed briefly in dioxane under a nitrogen atmosphere to form, in 40% yield, the yellow, crystalline *syn*-(benzonorbornadiene)-tricarbonylchromium, 83, mp 132°. Hydroboration-oxidation



(25)

81 82 83

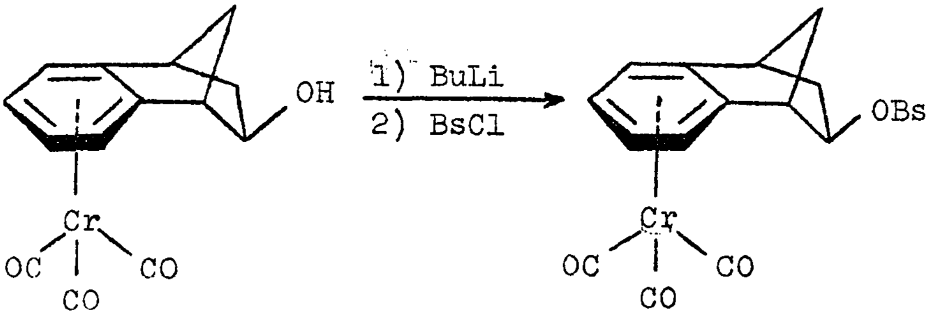
gave a good yield (70%) of the *syn*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium, 84, mp 148° (dec.). Subsequent



(26)

83 84

treatment with n-butyl lithium and bromobenzenesulfonyl chloride gave the *syn*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium, 85, mp 127° (dec), in 43% yield.

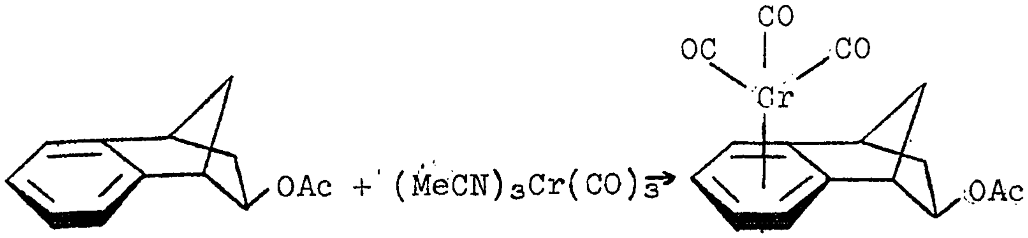


(27)

84 85

Anti-(benzonorbornen-2(exo)-yl bromobenzenesulfonate)tricarbonylchromium

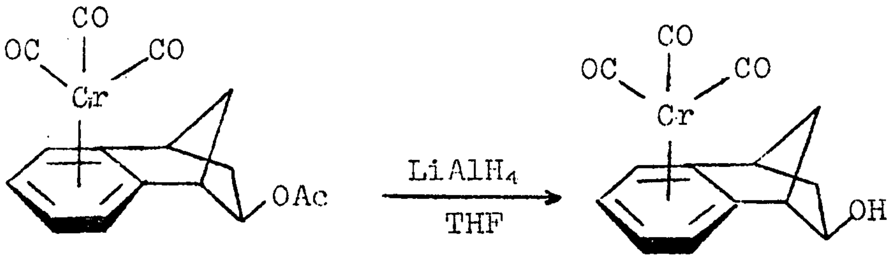
A mixture of benzonorbornen-2(exo)-yl acetate, 86, and (triacetonitrile)tricarbonylchromium, 82, were heated at reflux in dioxane for a few hours under nitrogen to form in 41% yield, the yellow, crystalline, anti-(benzonorbornen-2(exo)-yl acetate)tricarbonylchromium, 87, mp 150-152°.



(28)

86 82 87

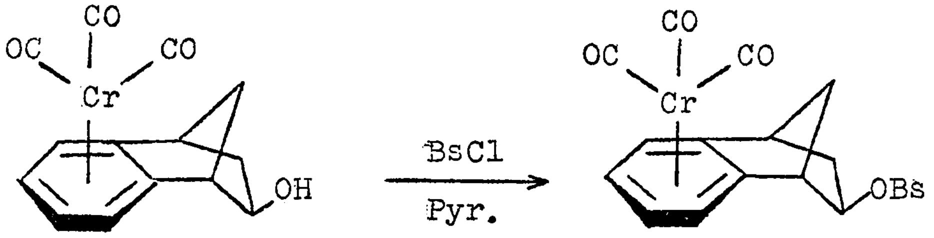
Reduction of the acetate, 87, with lithium aluminum hydride gave the alcohol, anti-(benzonorbornen-2(exo)-yl)-tricarbonylchromium, 88, mp 130-132°, in 59% yield.



(29)

87 88

Treatment of the alcohol, **88**, with bromobenzenesulfonyl chloride in pyridine gave *anti*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium, **89**, mp ~148°.

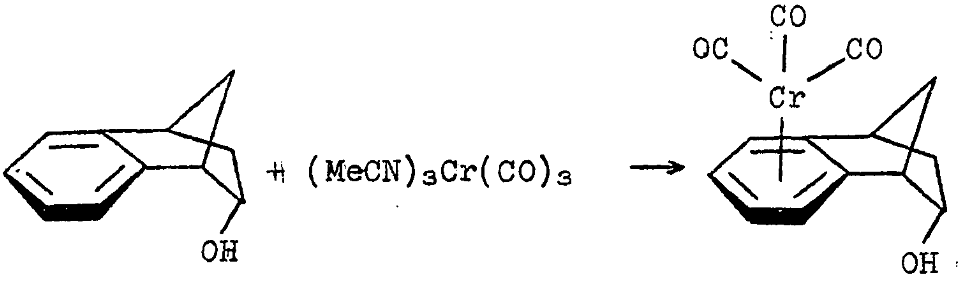


(30)

88 **89**

Anti-(benzonorbornen-2(*endo*)-yl bromobenzenesulfonate)tricarbonylchromium

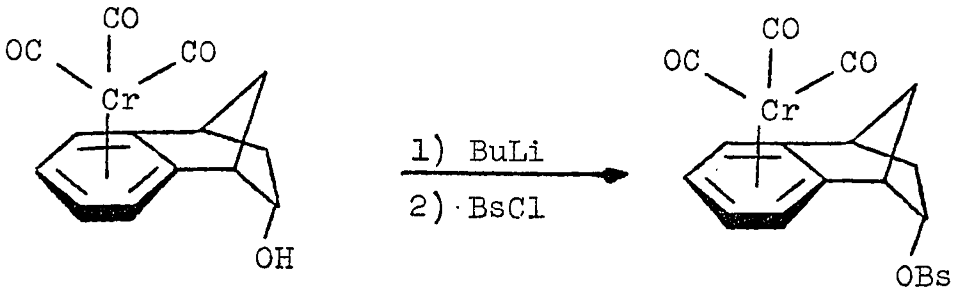
A mixture of benzonorbornen-2(*endo*)-ol, **90**, and (triacetonitrile)tricarbonylchromium, **82**, were refluxed briefly under nitrogen to form what was presumably the *anti*-(benzonorbornen-2(*endo*)-ol)tricarbonylchromium, **91**, mp 135-137°, in 28% yield.



(31)

90 **82** **91**

Treatment of the alcohol, **91**, with n-butyl lithium and bromobenzenesulfonyl chloride leads to *anti*-(benzonorbornen-2(*endo*)-yl bromobenzenesulfonate)tricarbonylchromium, **92**, mp 170° (dec), in 25% yield.



(32)

91 **92**

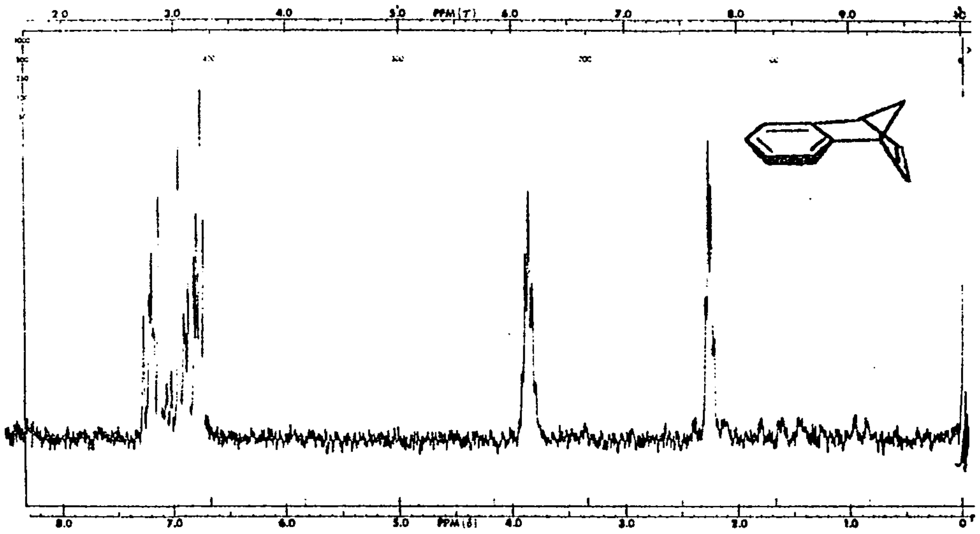
Proof of stereochemistry of (benzonorbornen-2-yl bromobenzenesulfonate)tricarbonylchromiums

Complexation of benzonorbornadiene (Equation 25) The nmr spectra of benzonorbornadiene, **81**, and its tricarbonylchromium complex, **83**, in deuterochloroform, Figures 19 and 20, reveal small differences in the non-aromatic chemical shifts of the two compounds (Table 22).

Clearly the largest effect is upon the aromatic absorption; there always is, in general, a shift of about 100 Hz upfield upon complexation (3, 4, 5, 6, 7). Otherwise, the effects are relatively small (Table 23).

Figure 19. A-60 nmr spectrum of benzonorbornadiene in deuterochloroform

Figure 20. A-60 nmr spectrum of *syn*-(benzonorbornadiene)tricarbonylchromium in deuterochloroform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4.0
5.0
PPM (τ)
6.0
7.0
8.0
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10
8.0
7.0
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3.0
2.0
1.0
0

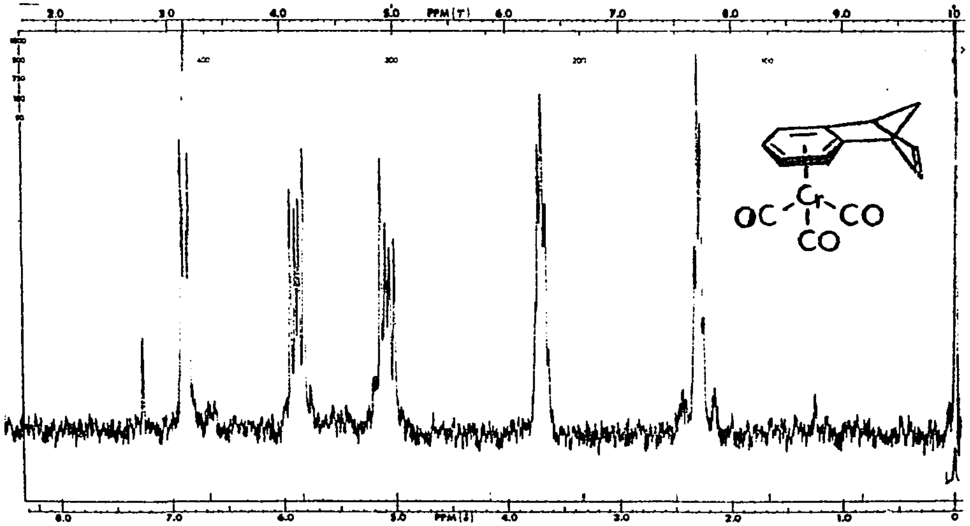
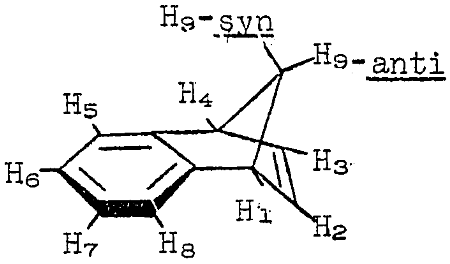

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
Cr
OC
CO
CO
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Table 22. The chemical shifts of benzonorbornadiene, *syn*-(benzonorbornadiene)tricarbonylchromium, and *anti*-(benzonorbornadiene)tricarbonylchromium in deuterochloroform and benzene[a]



Compound	Solvent	$H_{5,6,7,8}$	$H_{1,4}$	$H_{2,3}$	H_9-*syn*[b]	H_9-*anti*[b]
Free arene (81)	$CDCl_3$	424	232	407	135	
	ØH	420[c]	217	396	128	
syn-complex (83)	$CDCl_3$	328	221	411	138	
	ØH	288	182	402	105	
anti-complex (93)	$CDCl_3$	318	222	398	148	128
	ØH	275	186	367	146	103

[a] Shifts given in Hz downfield from tetramethylsilane; 60 megacycle spectrometer.

[b] Assignments made on basis of "W-effect" (65); the downfield portion of the methano AX pattern showed more multiplicity.

[c] Estimated maximum error ±5 Hz.

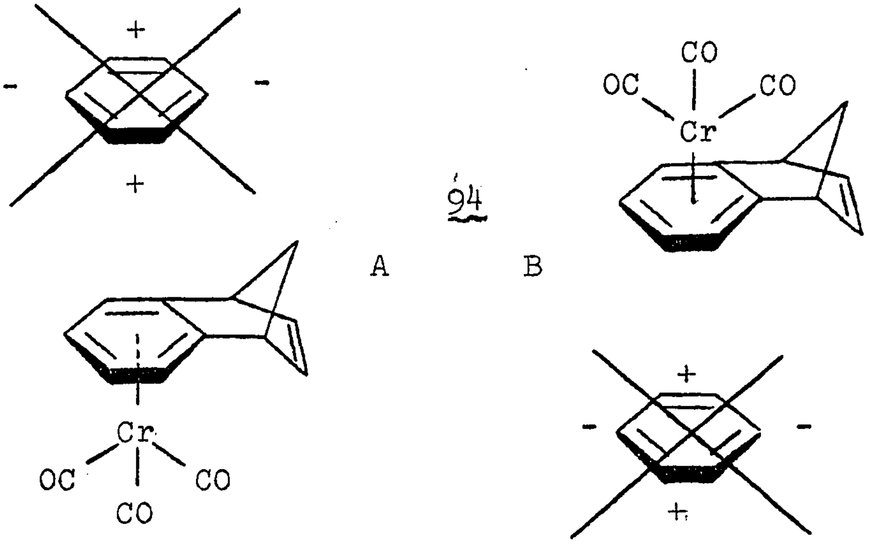
Table 23. The chemical shift change experienced by benzonorbornadiene absorptions upon complexation[a]

Isomer	Solvent	$H_{5,6,7,8}$	$H_{1,4}$	$H_{2,3}$	H_9-*syn*	H_9-*anti*
syn-complex (83)	$CDCl_3$	-96	-11	4	3	
	ØH	-132[b]	-35	6	-23	
anti-complex (93)	$CDCl_3$	-106	-10	-9	13	- 7
	ØH	-145[b]	-31	-29	18	-25

[a] Values calculated by subtracting the norbornadiene absorption from that for the tricarbonylchromium complex (Table 22). Thus a negative value means an upfield shift upon complexation.

[b] Estimated maximum error ±5 Hz.

The spectral absorptions of (arene)tricarbonylchromiums undergo abnormally large upfield shifts in benzene (4) presumably because the electron deprived nature of the complexed arene gives rise to a loose complex with the basic benzene solvent molecules. If model 94 is invoked for this association one might expect the two bridges to experience quite different shifts resulting from the quite different orientation of those bridges to the benzene solvent molecules. The spectra of norbornadiene, 81,



94

A B

and its tricarbonylchromium complex, 83, in benzene are shown (Figures 21 and 22). From the shifts in benzene and in deuterochloroform (Table 22), one can calculate the solvent shift for the free and complexed systems (Table 24).

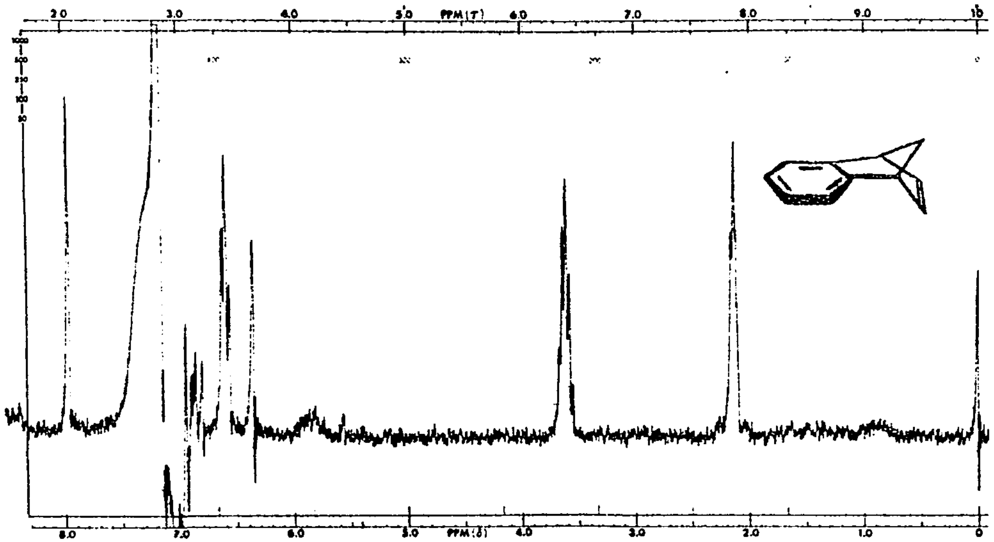
Table 24. The effect of solvent benzene on the deuterochloroform chemical shift of benzonorbornadiene and its tricarbonylchromium complexes[a]

Compound	$H_{5,6,7,8}$	$H_{1,4}$	$H_{2,3}$	H_9-*syn*	H_9-*anti*
Free arene (81)	-4	-15	-11		-7
syn-complex (83)	-40	-39	- 9		-33
anti-complex (93)	-43	-36	-31	-2	-25

[a] Values calculated by subtracting shift in deuterochloroform from shift in benzene (Table 22).

Figure 21. A-60 nmr spectrum of benzonorbornadiene in benzene

Figure 22. A-60 nmr spectrum of _syn_-(benzonorbornadiene)tricarbonylchromium in benzene


PPM(τ)
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3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
PPM(δ)
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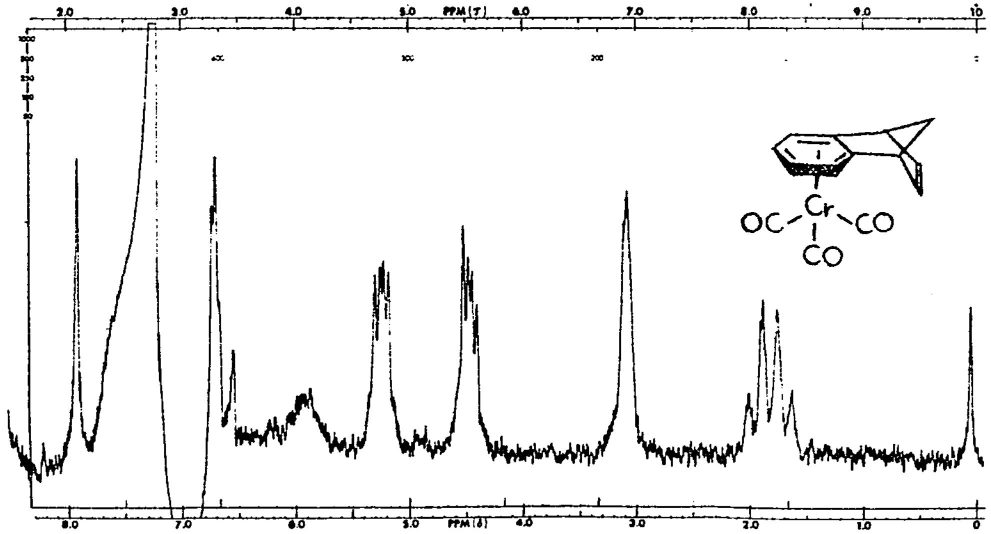
3.0
2.0
1.0
0

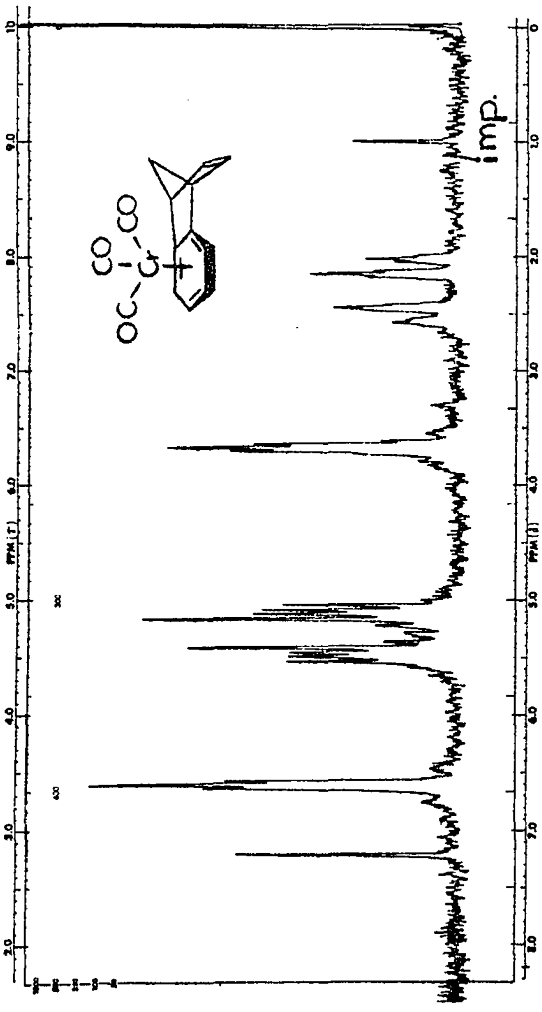

PPM(τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
OC
Cr
CO
CO
PPM(δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

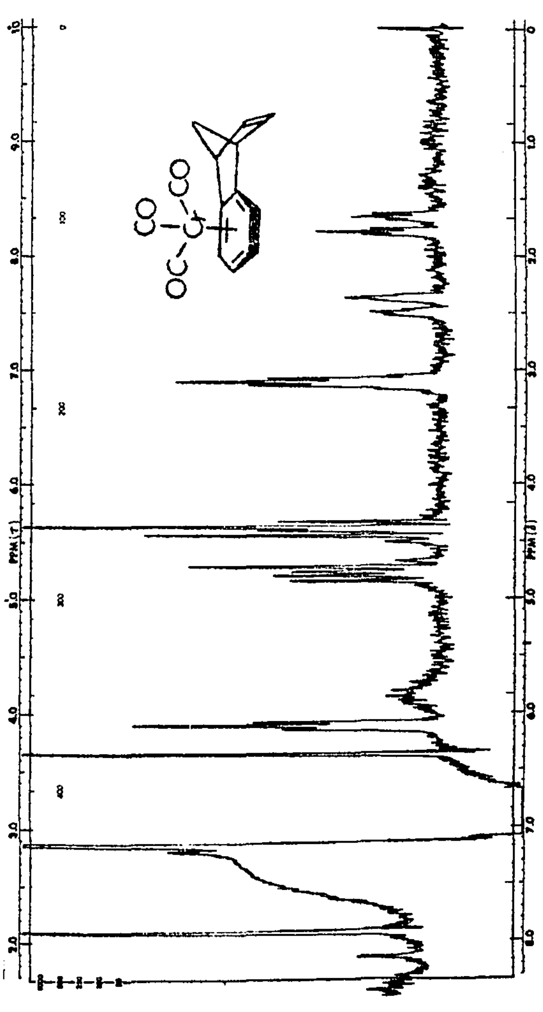
As expected *a priore*, the benzene solvent shift for the aromatic protons of the *syn*-complex is much higher than for the free arene. Moreover, the bridgehead protons, because they lie in the benzene plane, also experience the greater upfield shift in the *syn*-complex. What is particularly interesting, however, is the fact that the absorptions of the etheno protons undergo similar upfield shifts in the free and *syn*-complexed arene, while the absorptions of the methano protons of the *syn*-complex experience significantly higher upfield shifts, -33 Hz, compared to -7 Hz for the free arene (Table 24). This phenomenon is more consistent with solvent-solute model, **94**A, but confirmation of our assignment lies in the examination of the spectra of the isomer of **83**.

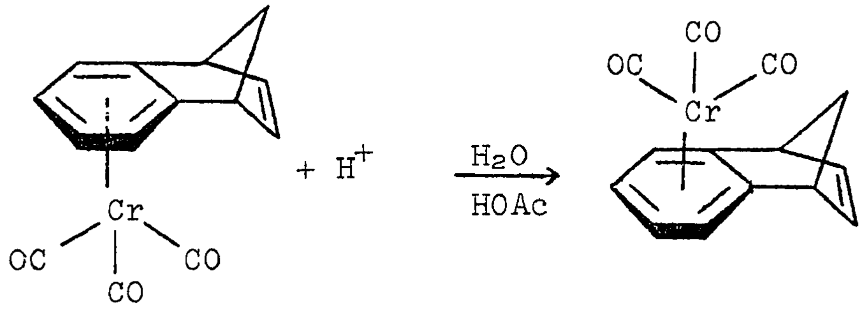
The tricarbonylchromium complex of benzonorbornadiene formed in Equation 25 and tentatively assigned, on the basis of solvent shift, the *syn* stereochemistry, was subjected to a catalytic amount of strong acid in acetic acid and with enough dioxane to bring the mixture into solution. The product, **93**, yellow and crystalline, mp 127.5-129.5°, was formed in 11% yield. Its nmr spectrum in deuterochloroform, Figure 23, while consistent with a tricarbonylchromium complex of benzonorbornadiene, shows

Figure 23. A-60 nmr spectrum of _anti_-(benzonorbornadiene)tricarbonylchromium in deuterochloroform

Figure 24. A-60 nmr spectrum of _anti_-(benzonorbornadiene)tricarbonylchromium in benzene


OC
CO
CO
Cr
imp.
PPM (τ)
PPM (δ)


OC
CO
CO
Cr
PPM (τ)
PPM (δ)



(33)

83

93

a striking contrast to that of *syn*-isomer; the methano protons, an AB multiplet in the *syn*-isomer (Figure 20) approaches an AX pattern in the *anti*-isomer; the adjacent metal has displaced the H_9-*anti* and H_9-*syn* absorptions about equally either side of their absorption in the *syn*-isomer, where the metal could not directly perturb them. Assignment of shifts (Table 22) in these solvents allows determination of the effect of solvent on the chemical shifts of the *anti*-isomer (Table 24).

This isomer of 83 behaves similarly to the *syn*-complex as far as the effect of benzene (Figure 24) upon the aromatic and bridgehead absorptions are concerned (Table 24). The etheno and methano protons behave oppositely in the two isomers. While the etheno bridge protons of the isomer of 83 undergo large upfield shifts (-31 Hz), they are shifted less in the *syn*-isomer (-9 Hz). On the other hand, while the methano absorptions in the *syn*-isomer undergo a large shift (-33 Hz), they are shifted less, on the average, in its isomer (average is -14 Hz).

It is important to note that free benzonorbornadiene undergoes moderate upfield shifts in benzene; this quite general phenomenon cannot be, probably, the result of a specific solvent-solute complex, but rather, the result of the diamagnetic anisotropy of benzene acting in a random fashion (66). Consequently, subtraction of the benzene solvent shifts for the free arene from these for the complexes should reveal effects that are an effect solely of the specific solvent-solute interaction model we proposed (94). The results of this calculation are presented in Table 25.

The effect of either *syn*- or *anti*-complexation is to make for a similar solvent shift on the aromatic absorption, about -40 Hz, and on the bridgehead proton absorption, about -20 Hz, indicating that the stereochemistry of the metal, as one would expect, does not affect the solvent shift on protons lying on the benzene plane.

The fact that the $H_{2,3}$ absorptions experience a negligible (2 Hz) solvent shift upon *syn*-complexation and a -20 Hz shift upon *anti*-complexation is consistent with model 94B for the *anti*-isomer.

Table 25. The effect of solvent benzene *vs.* deuterochloroform upon the chemical shift change experienced by benzonorbornadiene upon complexation[a]

Isomer	$H_{5,6,7,8}$	$H_{1,4}$	$H_{2,3}$	H_9-*syn*	H_9-*anti*
syn-complex (83)	-36[b]	-24	2	-26	
anti-complex (93)	-39[b]	-21	-20	5	-18

[a] Values for a particular isomer are calculated by subtracting the chemical shift change experienced by benzonorbornadiene absorption upon complexation in deuterochloroform from that in benzene (Table 24).

[b] Estimated maximum error ±5 Hz.

Whereas both methano protons undergo a -26 Hz solvent shift incurred upon *syn*-complexation, 83, the same protons go their separate ways in the *anti*-isomer; the 9-*syn* proton in the *anti*-isomer, 93, experiences a positive solvent shift (5 Hz) while the 9-*anti* proton experiences a -18 Hz solvent effect. The 9-*syn* proton behavior for the *anti*-isomer is quite consistent with model 94B, since the solvent benzene molecule could not approach the sterically inaccessible proton. The 9-*anti* proton solvent shift of -18 Hz upon *anti*-complexation is not, at this time, understood.

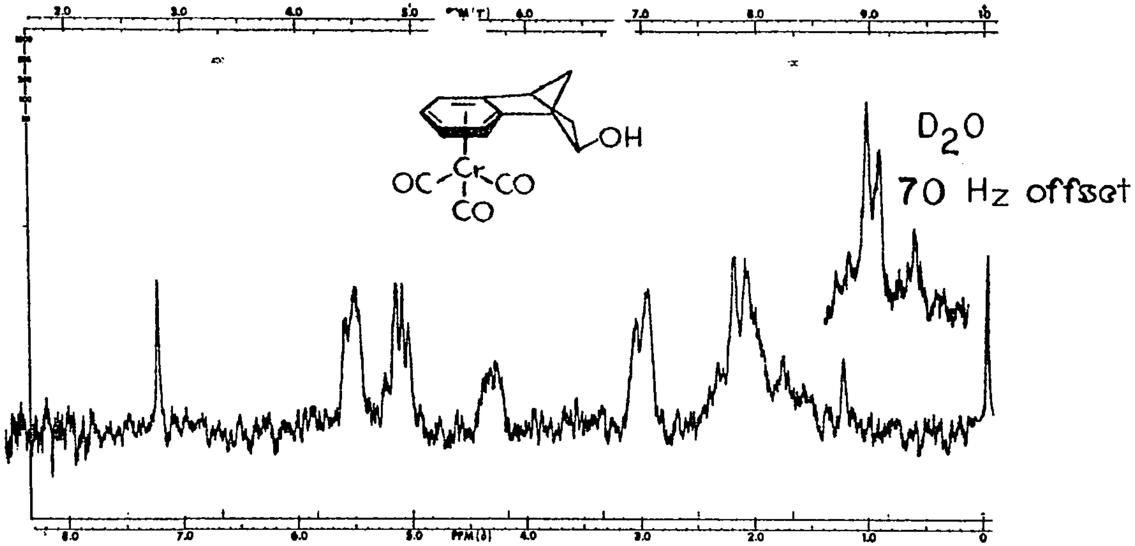
Hydroboration of syn-(benzonorbornadiene)tricarbonylchromium Since the hydroboration of free benzonorbornadiene gives the *exo*-alcohol (67), **95**, the yellow, powdery product of the hydroboration-oxidation of the *syn*-(benzonorbornadiene)tricarbonylchromium (Equation 26) is given the *syn*-*exo* assignment, **84**. The nmr spectrum (Figure 25) is different than that of *anti*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium (Figure 26), and is consistent with the benzonorben-2(*exo*)-ol skeleton.

Sulfonation of the syn-(benzonorborene-2(exo)-ol)tricarbonylchromium The brosylation step (Equation 27) gave a yellow crystalline material, mp 170° (dec), whose mass spectrum (*m/e* 514, 516), and solvolytic behavior (*vide infra*) upheld the assignment of *syn*-*exo* brosylate, **85**. Just as importantly, its nmr (Figure 27) resembled that of *syn*-(benzonorbornen-2(*exo*)-yl acetate)tricarbonylchromium (Figure 28), whose stereochemistry was affirmed below.

Syn- and anti-(benzonorboren-2(exo)-yl acetate)tricarbonylchromium The treatment of *syn*-(benzonorbornadiene)tricarbonylchromium, **83**, with mineral acid in the presence of acetic acid, besides forming the *anti*-(benzonorbornadiene)tricarbonylchromium, **93**, also forms a yellow crystalline material, mp 143.5-146.0°, in 5% yield. While

Figure 25. A-60 nmr spectrum of _syn_-(benzonorbornen-2(_exo_)-ol)tricarbonylchromium in deuterochloroform

Figure 26. A-60 nmr spectrum of _anti_-(benzonorbornen-2(_exo_)-ol)tricarbonylchromium in deuterochloroform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4.0
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6.0
7.0
8.0
9.0
10
OH
OC
Cr
CO
CO
D_2O
70 Hz offset
PPM (δ)
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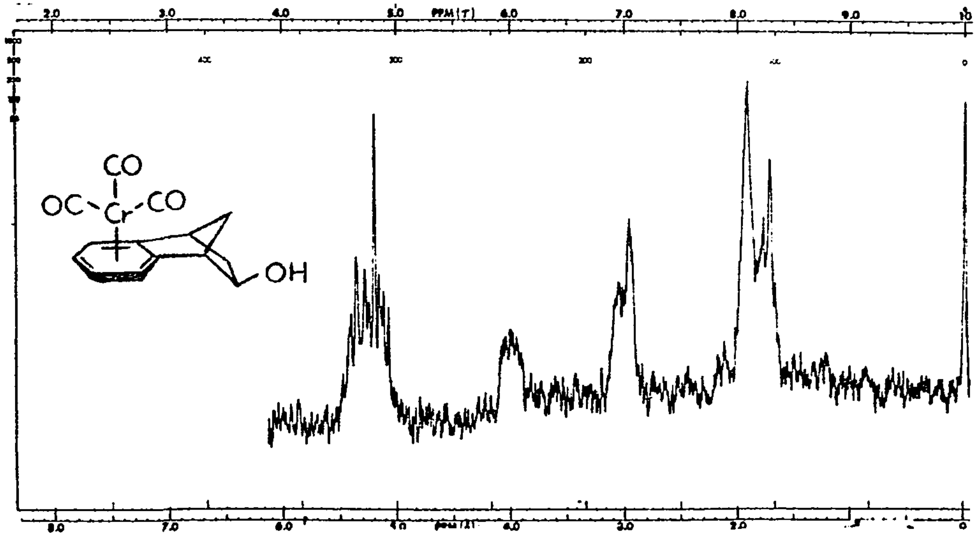
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


PPM (τ)
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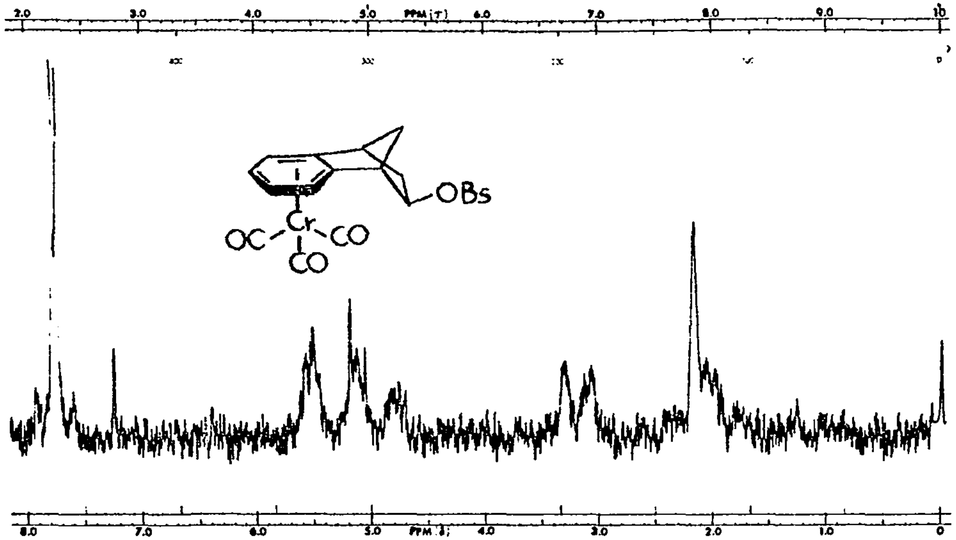
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
CO
OC
Cr
CO
OH
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0

Figure 27. A-60 nmr spectrum of *syn*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium in deuterochloroform

Figure 28. A-60 nmr spectrum of *syn*-(benzonorbornen-2(*exo*)-yl acetate)-tricarbonylchromium in deuterochloroform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Cr
OC
CO
CO
PPM (τ)
PPM (δ)
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4.0
5.0
6.0
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2.0
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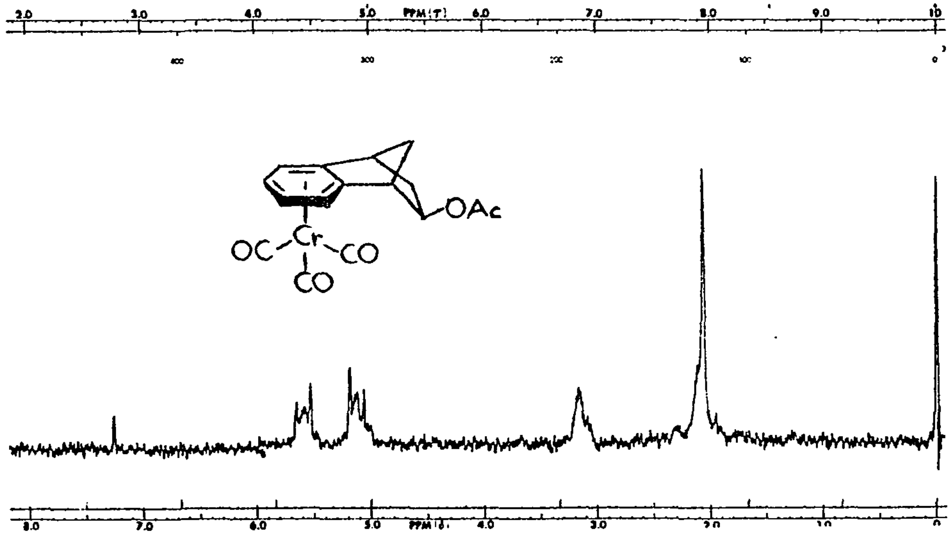
OAc
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CO
CO
PPM (τ)
PPM (δ)
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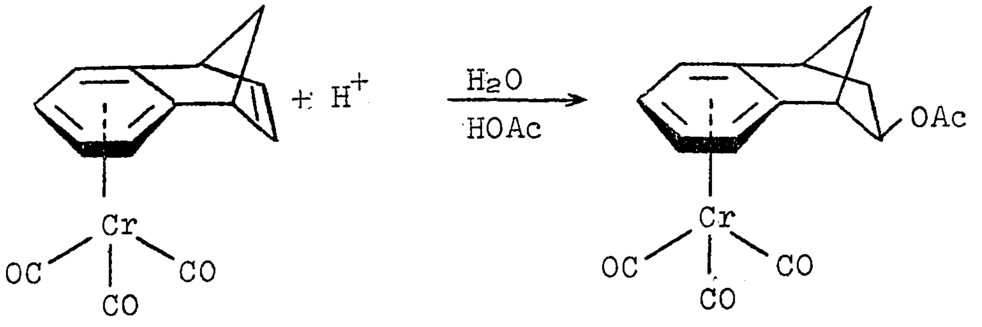


(34)

83

96

the nmr (Figure 28) was consistent with a tricarbonylchromium complex of benzonorbornen-2-yl acetate, the assignment was, *a priore*, one of four possibilities.

To facilitate the study, the nmr spectrum, Figure 29, of another acetate isomer, 87, (Equation 28) was examined. It was clearly different than that for 96. The nmr solvent method, which worked well in the case of the benzonorbornadiene complexes, was applied here (Tables 26, 27, and 28 contain data derived from Figures 28-33). The final results, Table 28, are considered. Errors generally prohibit the use of any data except for that on the 2-hydrogen, which undergoes an -18 Hz shift in the *anti-exo* isomer, 87, as a result of the solvent-solute complex, 97B, while the shift for the 2-hydrogen in the *syn-exo*

Figure 29. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*exo*)-yl acetate)-tricarbonylchromium in deuterochloroform

Figure 30. A-60 nmr spectrum of *syn*-(benzonorbornen-2(*exo*)-yl acetate)-tricarbonylchromium in benzene

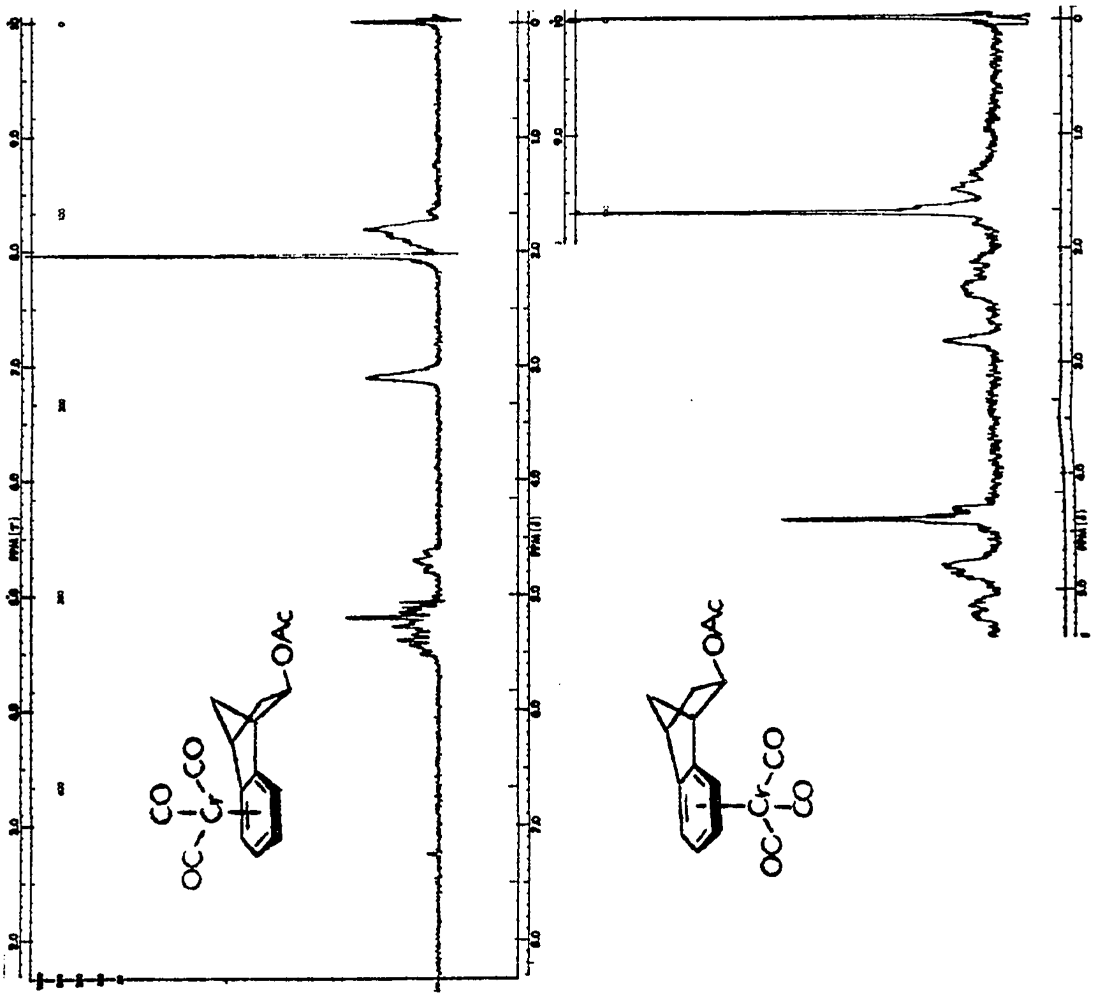
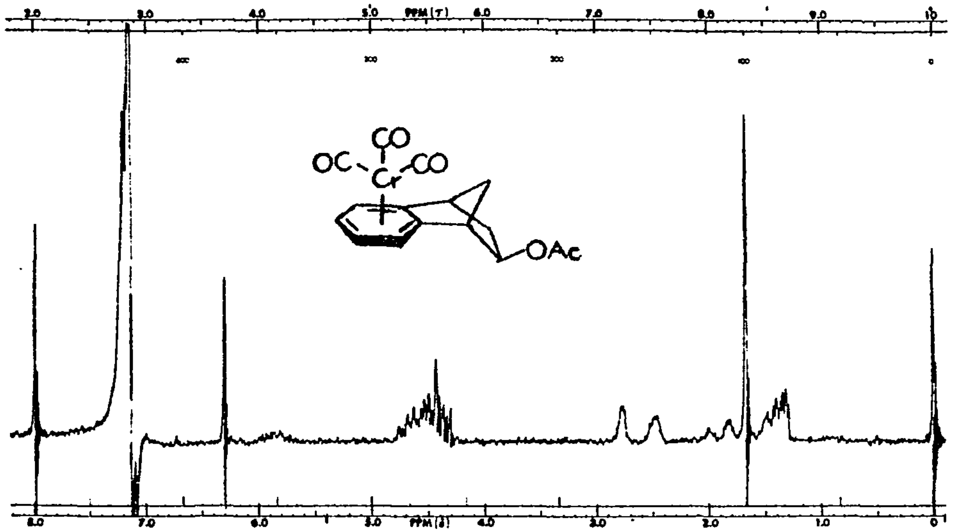

OAc
CO
OC
Cr
CO
OAc
OC
Cr
CO
CO

Figure 31. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*exo*)-yl acetate)-tricarbonylchromium in benzene

Figure 32. A-60 nmr spectrum of benzonorbornen-2(*exo*)-yl acetate in deuterochloroform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5.0
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10
OC
Cr
CO
CO
OAc
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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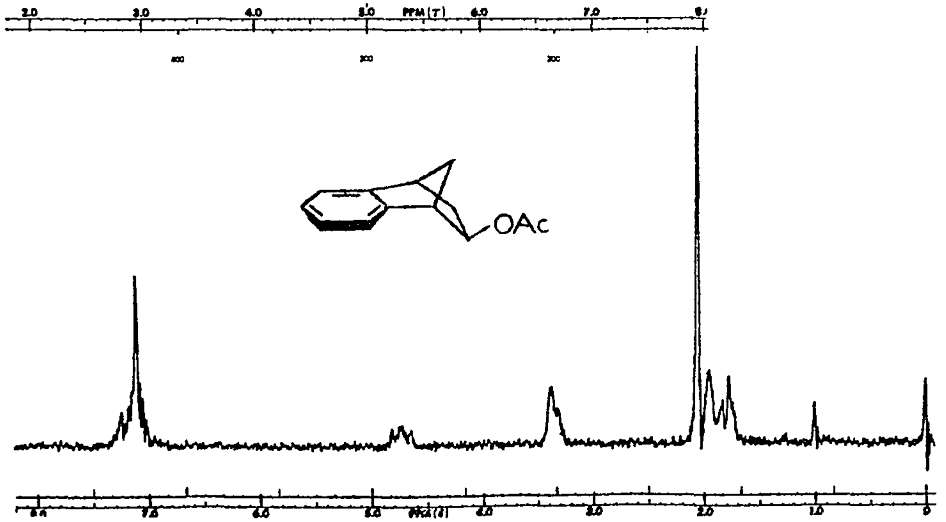
PPM (τ)
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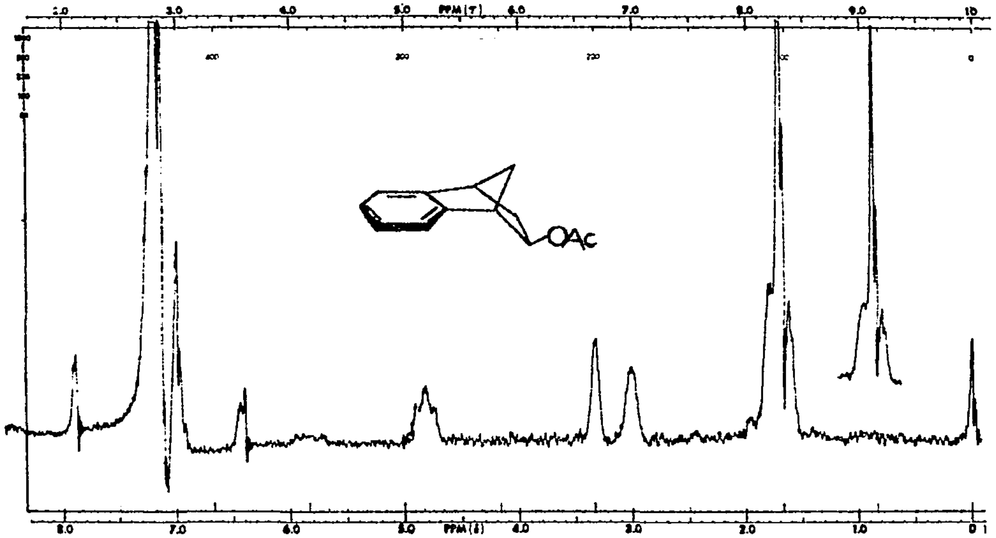
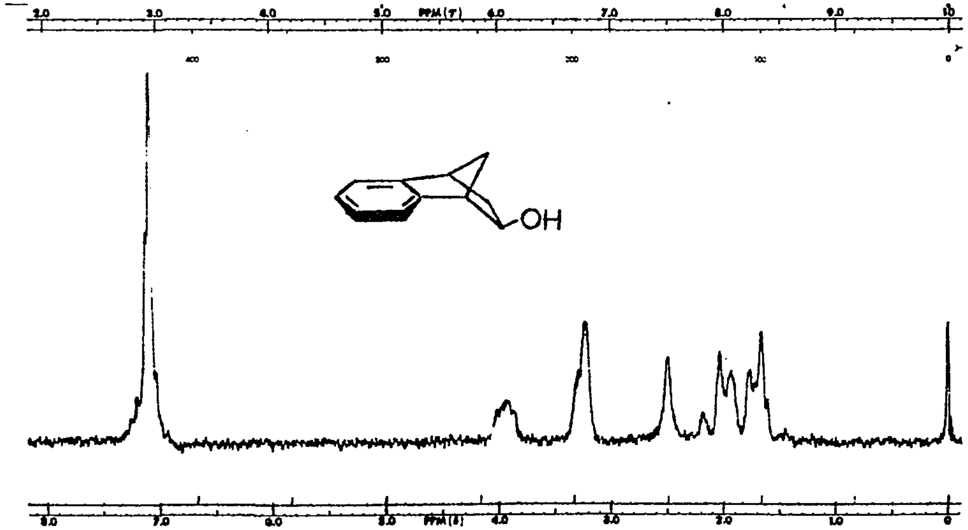
3.0
4.0
5.0
6.0
7.0
8.0
OAc
PPM (δ)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

Figure 33. A-60 nmr spectrum of benzonorbornen-2(_exo_)-yl acetate in benzene

Figure 34. A-60 nmr spectrum of benzonorbornen-2(_exo_)-ol in deuterochloroform



PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
OAc
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0



PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
OH
PPM (δ)
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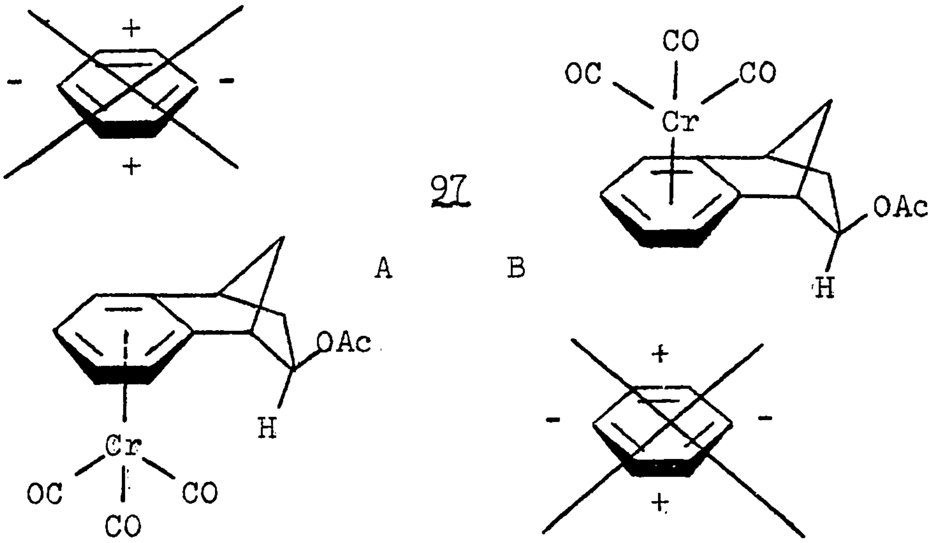
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

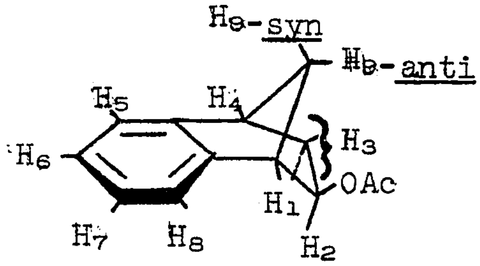


97

A B

isomer, **96**, is only -1 Hz. The stereochemistry of the tricarbonylchromium is confirmed as *syn* for **96** and *anti* for **87** but that of the acetate group in the *syn*-complex, **96**, deserves consideration. We could not, *a priori*, predict whether the product of Equation 34 would possess *exo* or *endo* acetate. To resolve this question we note the downfield shift (13 Hz) effected upon the *syn*-9-hydrogen by *anti*- but not *syn*-complexation of benzonorbornadiene (Table 22); moreover the *anti*-9-hydrogen is shifted upfield (-7 Hz) in *anti*-, but not *syn*-complexation. If, therefore, those methano and ethano bridge protons which are over the benzene ring (the methano proton over the benzene ring is the $H_{9\text{-}syn}$ proton, while the ethano proton over the benzene ring is the H_2-*endo* proton) are equally sensitive to

Table 26. The chemical shifts of benzonorbornen-2(exo)-yl acetate, syn-(benzonorbornen)-2(exo)-yl acetate tricarbonylchromium, and anti-(benzonorbornen-2-(exo)-yl acetate)tricarbonylchromium in deuterochloroform and benzene[a]



Compound	Solvent	$H_{5,6,7,8}$	$H_{1,4}$	H_2	H_3	H_9	OAc
exo-acetate (86)	$CDCl_3$	425	202	284	112[b]	112[b]	124
	ØH	425[c]	190	289	105[c]	105[c]	103
syn-complex (96)	$CDCl_3$	321	190	306	127[d]	127[d]	124
	ØH	276	169	310	139[d] or	94[d]	102
anti-complex (87)	$CDCl_3$	318	188	283	112[c]	112[c]	123
	ØH	270[c]	157	270[d]	105[c] or	83[c]	100

[a] Shifts given in Hz downfield from tetramethyl silane; 60 megacycle spectrometer.

[b] Estimated maximum error ± 7 Hz.

[c] Estimated maximum error ± 5 Hz.

[d] Estimated maximum error ± 10 Hz.

Table 27. The effect of solvent benzene on the chemical shifts of benzonorbornen-2(*exo*)-yl acetate and its tricarbonylchromium complexes[a]

Compound	$H_{5,6,7,8}$	$H_{1,4}$	H_2	H_3	H_9	OAc
exo-OAc (86)	0[b]	-12	5	-7[c]	-7[c]	-21
syn-*exo* (96)	-45	-21	4	12[d] or	-33[d]	-22
anti-*exo* (87)	-48[b]	-31	-13[e]	-7[c] or	-29[c]	-23

[a] Values calculated by subtracting shifts in deuterochloroform from shifts in benzene (Table 26).

[b] Estimated maximum error ± 5 Hz.

[c] Estimated maximum error ± 8 Hz.

[d] Estimated maximum error ± 13 Hz.

[e] Estimated maximum error ± 10 Hz.

proximity of the metal, the 22 Hz downfield shift of the 2-hydrogen incurred upon complexation to give what is presumed to be the *syn*-*exo* complex (Table 26, 86 and 96, in $CDCl_3$) and the lack of such change (-1 Hz) concurrent in the formation of the presumed *anti*-*exo* isomer (Table 26, 86 and 87, in $CDCl_3$) must be considered as firm support for the assignment of the product of Equation 34 as *syn*-(benzonorbornen-2(*exo*)-yl acetate)tricarbonylchromium, 96.

Table 28. The effect of solvent benzene *vs.* deuterochloroform upon the chemical shift experienced by benzonorbornen-2(*exo*)-yl acetate upon complexation[a]

Isomer	$H_{5,6,7,8}$	$H_{1,4}$	H_2	H_3	H_9	OAc
syn-*exo* (**96**)	-45^{b}	-9	-1	19^{c}	-26^{c}	-1
anti-*exo* (**87**)	-48^{d}	-19	-18^{e}	0^{f}	-22^{f}	-2

[a] Value for a particular isomer calculated by subtracting the chemical shift change experienced by benzonorbornen-2-(*exo*)-yl acetate absorption upon complexation in deuterochloroform from that in benzene (Table 27).

[b] Estimated maximum error ± 5 Hz.

[c] Estimated maximum error ± 15 Hz.

[d] Estimated maximum error ± 7 Hz.

[e] Estimated maximum error ± 10 Hz.

[f] Estimated maximum error ± 11 Hz.

Furthermore, models seem to rule out the *syn*-*endo* isomer, on steric grounds.

The resemblance of the spectrum (Figure 28) of this *syn*-*exo* acetate, **96**, to that of **85** (Figure 27) confirms the assignment previously made for the product of Equation 27, namely *syn*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium.

Reduction of anti-(benzonorbornen-2(exo)-yl acetate)-tricarbonylchromium The stereochemistry of the tricarbonylchromium upon attachment to benzonorbornen-2(*exo*)-yl acetate, 86, it has been shown, is *anti* (Equation 28). It would be expected that lithium aluminum hydride reduction (Equation 29) should not affect any isomerization, and this is shown to be the case by the nmr solvent method. Table 29 lists the shifts picked off the nmr spectra of benzonorbornen-2(*exo*)-ol, 95, in deuterochloroform (Figure 34), in benzene (Figure 35) and *anti*-(benzonorbornen-2(*exo*)-ol)-tricarbonylchromium, 88, in deuterochloroform (Figure 26), in benzene (Figure 36).

Table 29. The chemical shifts of benzonorbornen-2(*exo*)-ol, and *anti*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium[a, b]

Compound	Solvent	$H_{5,6,7,8}$	$H_{1,4}$	H_2	H_3	H_9	OH
exo-ol (95)	$CDCl_3$	424	195	235	120[c]	100[c]	150
	ØH	427	183	226	115[c]	95[c]	126
anti-*exo*-ol (88)	$CDCl_3$	311	180	239	101[d]	116[d]	115
	ØH	270	145	198	70[d]	104[c]	53

[a] Shifts given in Hz downfield from tetramethylsilane; 60 megacycle spectrometer.

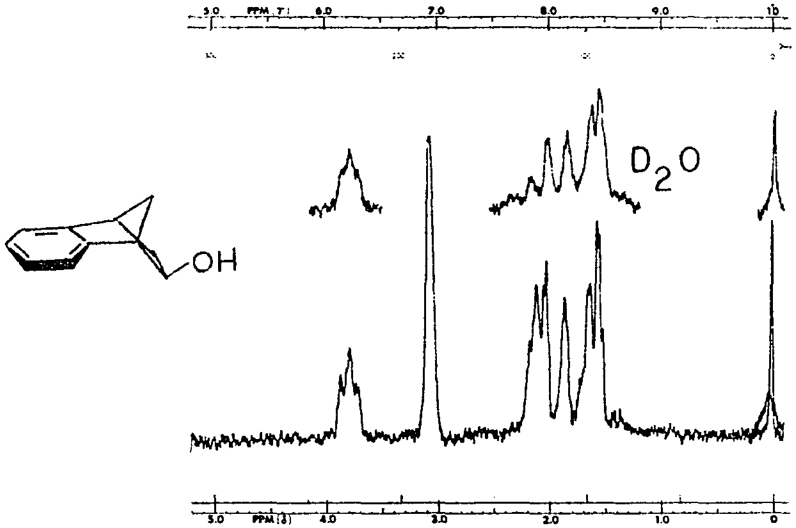
[b] See Table 26 for numbering of positions.

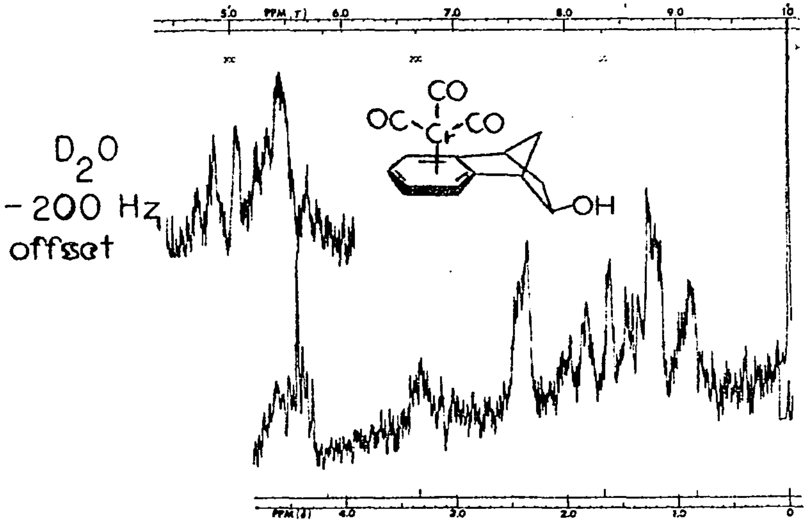
[c] Estimated maximum error ± 5 Hz.

[d] Estimated maximum error ± 10 Hz.

Figure 35. A-60 nmr spectrum of benzonorbornen-2(*exo*)-ol in benzene

Figure 36. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium in benzene


5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
D$_2$O
OH
5.0 PPM (δ) 4.0 3.0 2.0 1.0 0


5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
D$_2$O
-200 Hz
offset
CO
OC
Cr
CO
OH
PPM (δ) 4.0 3.0 2.0 1.0 0

Although uncertainty in assignment of 3-H and 9-H positions is large, there is an indication that complexation involves an upfield shift of the 3-H absorption and a downfield shift of the 9-H absorptions. The usual calculations on the absorptions leads one to consider the effect of specific solute-solvent interaction (Table 30).

Table 30. The effect of solvent benzene *vs.* deuterochloroform upon the chemical shift experienced by benzonorbornen-2(*exo*)-ol upon *anti*-complexation[a]

$H_{5,6,7,8}$	$H_{1,4}$	H_2	H_3	H_9	OH
-44	-23	-32	-26[b]	-7[b]	-38

[a] Value for a particular isomer calculated by subtracting the chemical shift change experienced by benzonorbornen-2(*exo*)-ol absorption upon complexation in deuterochloroform from that in benzene (Table 29).

[b] Estimated maximum error ± 15 Hz.

The upfield shift on the 2-H and 3-H absorptions, and the lack of a significant one on the 9-H absorption, clearly indicates the isomer to be *anti*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium, **88**.

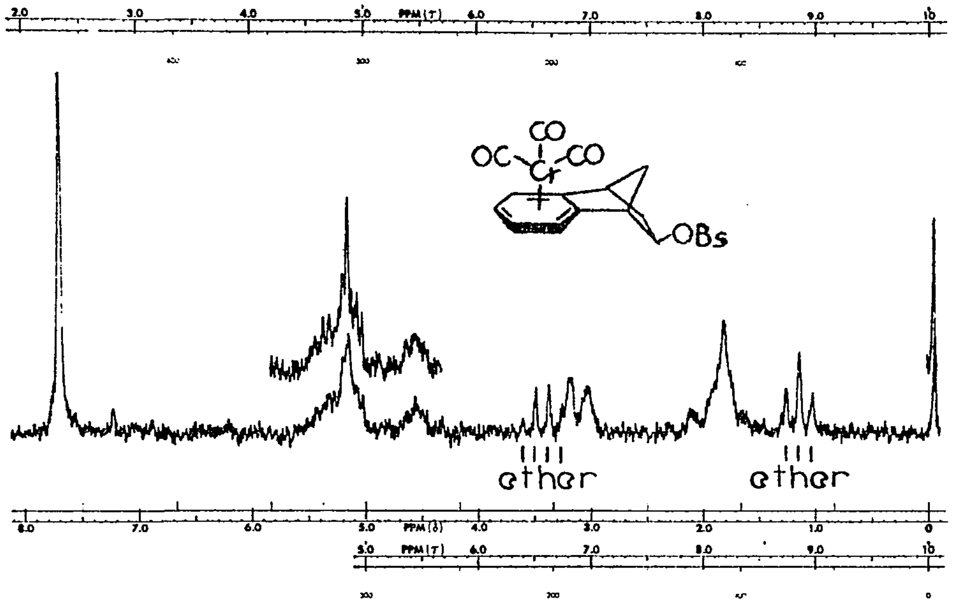
Brosylation of anti-(benzonorbornen-2(exo)-ol)tricarbonylchromium The product of sulfonation of the *anti*-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium, 88, (Equation 30) gave nmr spectra in deuterochloroform (Figure 37) and benzene (Figure 38) strongly resembling those for *anti*-(benzonorbornen-2(*exo*)-yl acetate)tricarbonylchromium, 87, (Figures 29 and 31). This, in addition to the mass spectrum (*m/e* 514, 516) and consistent solvolytic behavior (*vide infra*), supports the *anti*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium, 89, assignment.

Complexation of benzonorbornen-2(endo)-ol The stereochemical assignment for the product arising from the direct complexation of benzonorbornen-2(*endo*)-ol, 90 (Figure 31), is based strongly on analogy in lieu of any nmr spectra of the alcohol (this compound seemed more nearly insoluble than the other two isomers (*syn*-*exo* and *anti*-*exo*) and the nmr was quite noisy on the A-60 spectrometer).

We have seen how direct complexation of benzonorbornen-2(*exo*)-yl acetate, 86, gives the *anti*-isomer, 87 (Equation 28), and there is even more reason for benzonorbornen-2-(*endo*)-ol, 90, to give the *anti*-isomer, 91, considering the additional steric bulk brought to bear by the *endo*-hydroxy.

Figure 37. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium in deuterochloroform

Figure 38. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium in benzene


PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
CO
OC
CO
Cr
OBs
ether
ether
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

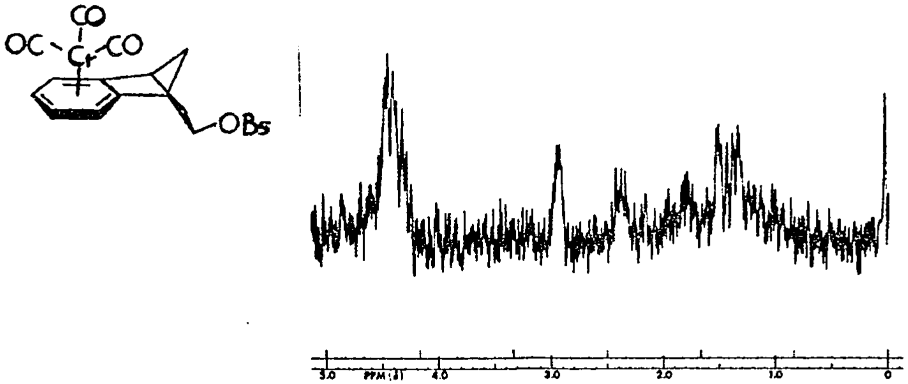
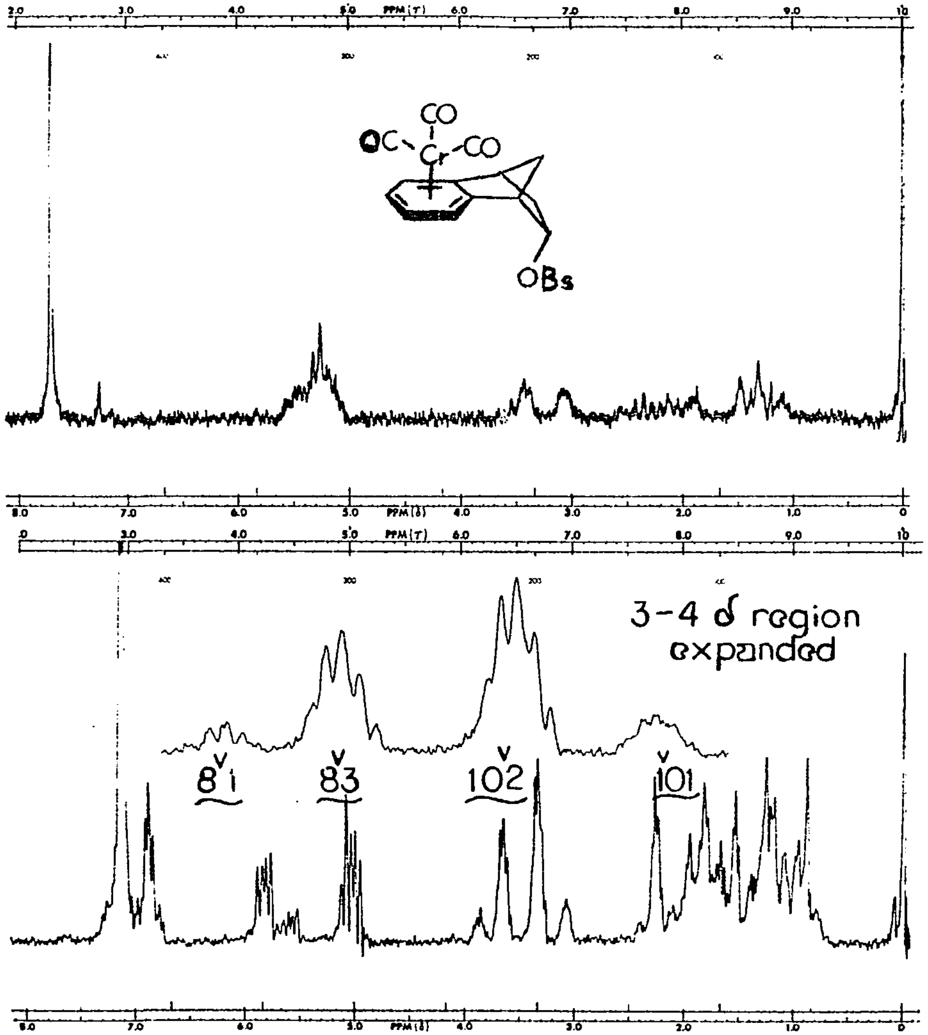

CO
OC
CO
Cr
OBs
PPM (δ)
5.0
4.0
3.0
2.0
1.0
0

Figure 39. A-60 nmr spectrum of *anti*-(benzonorbornen-2(*endo*)-yl bromobenzenesulfonate)tricarbonylchromium in deuterochloroform

Figure 40. A-60 nmr spectrum, in deuterochloroform, of product of hydrogenation of a mixture of benzonorbornadiene and *syn*-(benzonorbornadiene)-tricarbonylchromium



PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
CO
OC
Cr
CO
OBs
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3-4 δ region expanded
81
83
102
101

Brosylation of anti-(benzonorbornen-2(endo)-ol)tricarbonylchromium Obtained from the brosylation of the *anti*-*endo* alcohol, 91 (Equation 32) was a yellow crystalline material, mp 170° (dec), whose nmr in deuterochloroform (Figure 39) indicated an (arenyl brosylate)tricarbonylchromium that was neither the *syn*-*exo* brosylate, 85 (Figure 27), nor the *anti*-*exo* brosylate, 89, (Figure 37). Its mass spectrum (*m/e* 514, 516), solvolytic behavior (*vide infra*) and the suggested steric difficulty with *endo*-complexation lent credence to the assignment of *anti*-(benzonorbornen-2(*endo*)-yl bromobenzenesulfonate)tricarbonylchromium, 92.

Solvolyses

Solvolyses of the three isomeric complexed brosylates and the two uncomplexed brosylates in 70% aqueous acetone gave the following results (Table 31).

Product studies on the complexes were hindered, especially in the very slow solvolyzing system, by oxidation of the chromium(0) by water. Consequently, solvolysis of the rapidly ionizing *syn*-*exo* brosylate, 85, through 10 half-lives in 70% aqueous acetone gave 92% (by nmr) *syn*-*exo* alcohol, 84.

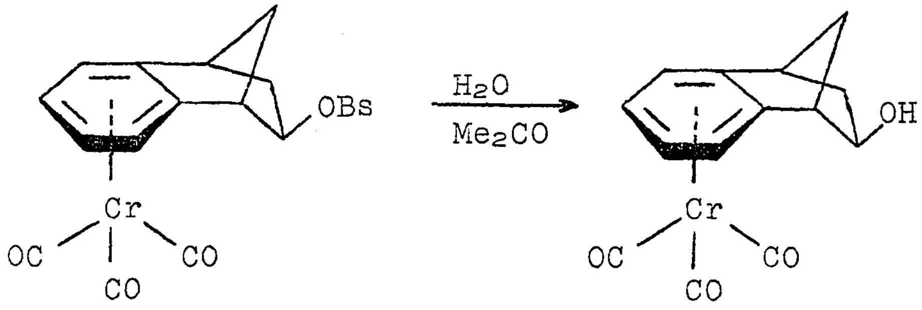
Table 31. Rates of solvolysis of free and complexed benzonorbornen-2-yl bromobenzenesulfonates in 70% aqueous acetone solution

Bromobenzenesulfonate		k(x10^4)^a				k_{rel} 80.0°
	40.9°	60.0°	80.0°	100.0°	120.2°	
Benzonorbornen-2(*exo*)-yl (98)	2.4	21	140			5800^c
Benzonorbornen-2(*endo*)-yl (99)			0.024	0.19	1.2	1.0^c
Anti-(benzonorbornen-2(*exo*)-yl)-tricarbonylchromium (89)			0.33	3.9		14
Syn-(benzonorbornen-2(*exo*)-yl)-tricarbonylchromium (85)		26^b	94			3900
Anti-(benzonorbornen-2(*endo*)-yl)-tricarbonylchromium (92)			0.016	0.065		0.67

[a] In sec^{-1}.

[b] k at 60.0°, in 80% aqueous acetone, is 6.91 x 10^{-4} sec^{-1}.

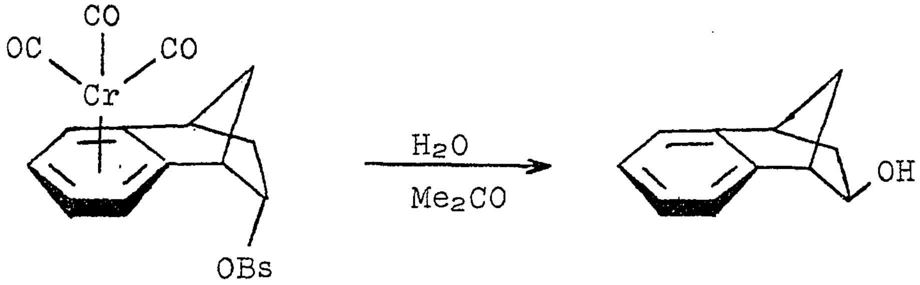
[c] Brown and Tritle (63) obtained an *exo/endo* ratio of 15000 at 25° in acetic acid.



(35)

85 84

Only uncomplexed *exo* alcohol, 95, was observed after about 3 half-lives (as calculated from the initial rate constant) of solvolysis of the *anti*-*endo* brosylate, 92, in 70% aqueous acetone.

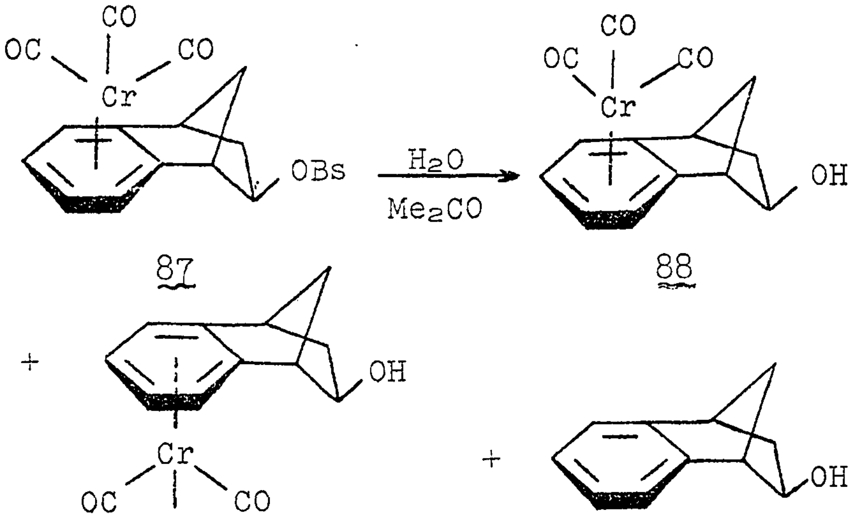


(36)

92 95

A mixture of free and complexed products was obtained from the solvolysis of the *anti*-*exo* brosylate, 89, in 70% aqueous acetone; of the complexed product (30%), nmr analysis tentatively concluded that about one-half was *anti*-*exo* alcohol, 88, and one-half *syn*-*exo* alcohol,

84. The free material was *exo* alcohol, **95**.



84 **95**

(37)

The near-unity relative rate for the *anti*-*endo* complex, **92**, solvolysis shows that the sum of torsional, steric, and field effects are small; the absence of a larger effect is consistent with the presumption that the benzene ring in benzonorbornen-2-yl systems is not electronically involved (with the exception of a small inductive effect) in *endo* brosylate solvolyses (**63**).

Anti-complexation, **89**, retards the solvolysis rate of the *exo* brosylate, **98**, by 400 fold. Tanida *et.al.* (64) have shown that the observed solvolysis rates of benzene-substituted benzonorbornen-2(*exo*)-yl bromobenzenesulfonates at 77.6° are related by the Hammett relationship $\log k/k_0 = \rho\sigma^+$, with the straight line possessing slope corresponding to $\rho = -3.26$. The σ^+ of groups incapable of electron release into electron deficient centers, such as NO_2, are closely approximated by their inductive parameters, σ^o. The tricarbonylchromium group possesses $\sigma^o = 0.82$ (13), and calculation of the effect of complexation on the solvolysis rate of the exo brosylate gives,

$$\log (k_{Cr(CO)_3}/k_o) = \rho\sigma^+ = -3.26 \times 0.82 = -2.67 \quad (38)$$

$$(k_{Cr(CO)_3}/k_o)_{calc.} = 2.14 \times 10^{-3} \quad (39)$$

This compares to the observed (Table 31),

$$(k_{Cr(CO)_3}/k_o)_{obs.} = 2.41 \times 10^{-3} \quad (40)$$

The effect of anti-complexation of the exo brosylate is then in line with the effect calculated on the basis of its inductive nature of the tricarbonylchromium group.

The exo/endo value, 21, for the solvolysis of the anti-complexes is the lowest yet attained for the solvolysis of phenyl-substituted benzonorbornen-2-yl bromobenzenesulfonates. Brown and Tritle (63) reported that the exo/endo value for the solvolysis of 6,7-(NO_2) benzonorbornen-2-yl bromobenzenesulfonate in acetic acid at 25° is 94.

Our low value is due to the fact that, whereas 6,7-(NO_2) substitution decreases the endo solvolysis by 25 times (63), substitution of tricarbonylchromium causes a mere 1.5 fold decrease; however, water oxidation of the anti-endo brosylate may have competed with solvolysis, so that the rate constant observed may have been largely that for the free *endo* brosylate.

Clearly, the fact that the *anti*-tricarbonylchromium group frustrates phenyl participation (63, 64) in the *exo* solvolysis rules out the "σ-π hyperconjugative" model, **77**.

Syn placement of the tricarbonylchromium group allows the solvolysis of the *exo* brosylate to proceed at nearly the rate of the unsubstituted *exo* brosylate. The tricarbonylchromium group should still exert its high electronegativity *syn*, so that special effects cause a 278 fold increase in the *exo* solvolysis over the rate at which the *anti*-*exo* solvolyzes. Two kinds of "special" effects are considered.

Steric acceleration Models show that a potential steric interaction between the tricarbonylchromium group and the ethano bridge in the *syn* complex, **85**, would be relieved if the *endo*-2-hydrogen were moved up simulating conversion to an sp^2 center. The question arises: is there enough steric acceleration to attainment of the carbonium ion to account for the rapid solvolysis of the *syn*-*exo* brosylate, **85**.

We have considered the olefin, **83**, containing two sp^2 centers, as a steric approximation to the carbonium ion, **100**, with one sp^2 center. Hydrogenation of the olefin, in introducing two sp^3 centers, resembles (probably exaggerates) the reverse of the solvolysis reaction, in which one sp^3 center is transformed into an sp^2 center (Chart 1).

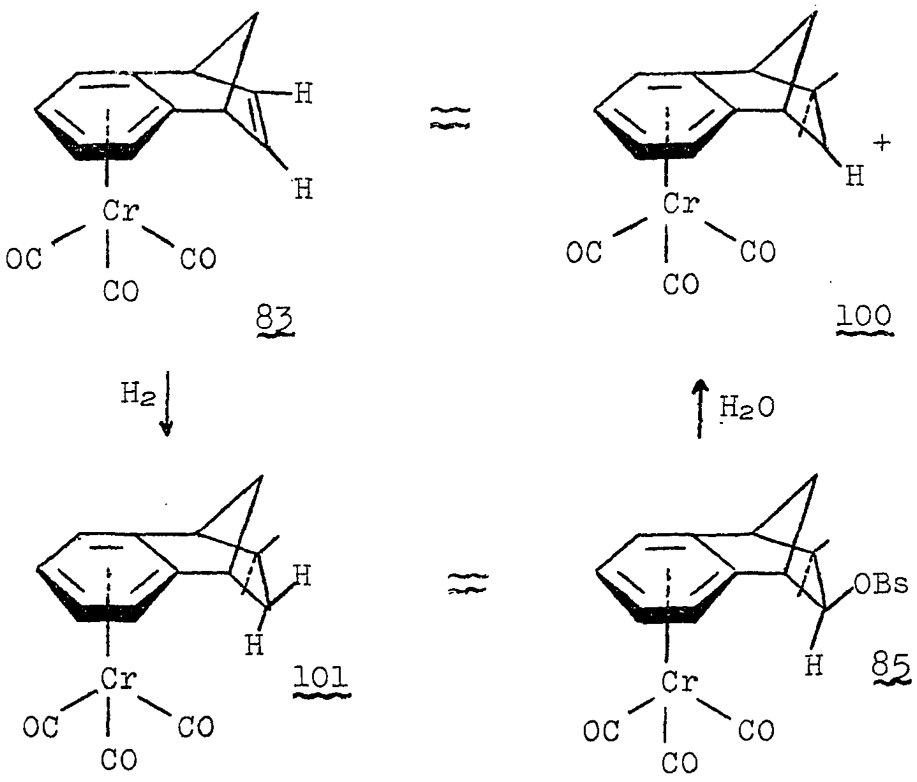


Chart 1. Syn-(benzonorbornadiene)tricarbonylchromium as a model for the syn-(benzonorbornen-2-yl)tricarbonylchromium cation

Thus the ratio of competitively hydrogenated benzonorbornadiene, **81**, and the *syn*-complex, **83**, might reflect the relative (corrected for the inductive effect of the tricarbonylchromium group) rates of solvolyses of benzonorbornen-2(*exo*)-yl bromobenzenesulfonate, **98**, and its *syn*-complex, **85**.

Relative rates of hydrogenation of benzonorbornadiene and its tricarbonylchromium complex A mixture of 0.750 mmoles benzonorbornadiene, **81**, and 0.597 mmoles *syn*-(benzonorbornadiene)tricarbonylchromium, **83**, were subjected to hydrogenation in acetic acid solution until it was calculated that 0.665 mmoles of hydrogen had been absorbed. The product was a mixture of benzonorbornadiene, **81**, benzonorbornene, **102**, *syn*-(benzonorbornadiene)tricarbonylchromium, **83**, and *syn*-(benzonorbornene)tricarbonylchromium, **101** (Table 32). The relative ratio of the products was assigned by integration of their respective bridgehead absorptions (Figure 40). Workup returned a ratio of free to complexed product, 1.265, which compares to 1.256 for the reactants: recovery was complete.

If the rate constants for absorption on the catalytic surface are about equal for the free and complexed arenes, as models permit one to assume, then the relative rates of hydrogenation should reflect only the relative concentrations of materials and the rate constants of the reduction

Table 32. Hydrogenation of a mixture of benzonorbornadiene and its *syn*-tricarbonylchromium complex

Compound	mmoles react.	mmoles prod.[a]
Benzonorbornadiene (81)	0.750	0.091
Benzonorbornene (102)		0.662
Syn-(benzonorbornadiene)-tricarbonylchromium (83)	0.597	0.439
Syn-(benzonorbornene)tricarbonylchromium (101)		0.155

[a] By nmr integration of bridgehead proton (Figure 40).

process, so that,

$$\frac{\text{Rate hydrogenation of } \underline{\text{syn}}\text{-complex}}{\text{Rate hydrogenation of free olefin}} = \frac{k_{\underline{\text{syn}}}}{k_{\text{free}}} \times \frac{[\underline{\text{syn}}]}{[\text{free}]} = \frac{\frac{d[\underline{\text{syn}}]}{dt}}{\frac{d[\text{free}]}{dt}} \qquad (41)$$

Integration yields

$$\frac{k_{\underline{\text{syn}}}}{k_{\text{free}}} = \frac{\ln([\underline{\text{syn}}]_o/[\underline{\text{syn}}]_f)}{\ln([\text{free}]_o/[\text{free}]_f)} \qquad (42)$$

where, at the end of the experiment there are concentrations of syn-complex, $[\underline{syn}]_f$, and free olefin, [free], compared to the starting concentrations of syn-complex, $[\underline{syn}]_o$, and free olefin, $[\text{free}]_o$. Expansion of Equation 42 gives,

$$\frac{k_{\underline{syn}}}{k_{\text{free}}} = \frac{\log\left(\frac{[\underline{syn}]_o/[\text{free}]_o}{[\underline{syn}]_f/[\text{free}]_f} \times \frac{[\text{free}]_o}{[\text{free}]_f}\right)}{\log\left([\text{free}]_o/[\text{free}]_f\right)} \tag{43}$$

From the values derived from Table 32,

$$[\underline{syn}]_o/[\text{free}]_o = 0.796 \tag{44}$$

$$[\text{free}]_o/[\text{free}]_f = 8.30 \tag{45}$$

$$[\underline{syn}]_f/[\text{free}]_f = 4.83 \tag{46}$$

Substitution yields

$$k_{\underline{syn}}/k_{\text{free}} = 0.140 \tag{47}$$

That is, the free olefin undergoes hydrogenation faster than the syn-complex by a factor of 7.17.

Because hydrogenation of benzonorbornadiene occurs on the exo side (65), the anti-complex should resemble the free olefin, as far as steric effects on the hydrogenation reaction are concerned. A mixture of 0.517 mmoles of anti- and 0.288 mmoles syn-complexed olefin were subjected to competitive hydrogenation (Table 33). Figure 41 and 42, the nmr spectra of crude and washed product, allow one to calculate, as before, that the rate constant for hydrogenation of the _anti_-complex that is 3 fold larger than for the _syn_-complex (Table 34).

Table 33. Hydrogenation of a mixture of _syn_- and _anti_-(benzonorbornadiene)tricarbonylchromium

Compound	mmoles react.	mmoles prod.[a]
Syn-(benzonorbornadiene)-tricarbonylchromium (83)	0.228	0.148
Syn-(benzonorbornene)tricarbonylchromium (101)		0.227
Anti-(benzonorbornadiene)-tricarbonylchromium (93)	0.517	0.130
Anti-(benzonorbornene)tricarbonylchromium (103)		0.240

[a] By nmr integration of bridgehead protons (Figure 42).

There is no doubt that the _syn_-tricarbonylchromium is hindering attainment of an sp^3 configuration on the C-2 and and C-3 positions, but whether this rate retardation (X 7.2) accounts for the effect of _syn_-tricarbonylchromium in the solvolysis reaction (Table 31) requires the

Figure 41. A-60 nmr spectrum, in deuterochloroform, of product of hydrogenation of a mixture of _syn_- and _anti_-(benzonorbornadiene)tricarbonylchromium

Figure 42. A-60 nmr spectrum, in deuterochloroform, of product of hydrogenation of a mixture of _syn_- and _anti_-(benzonorbornadiene)tricarbonylchromium; pentane washed

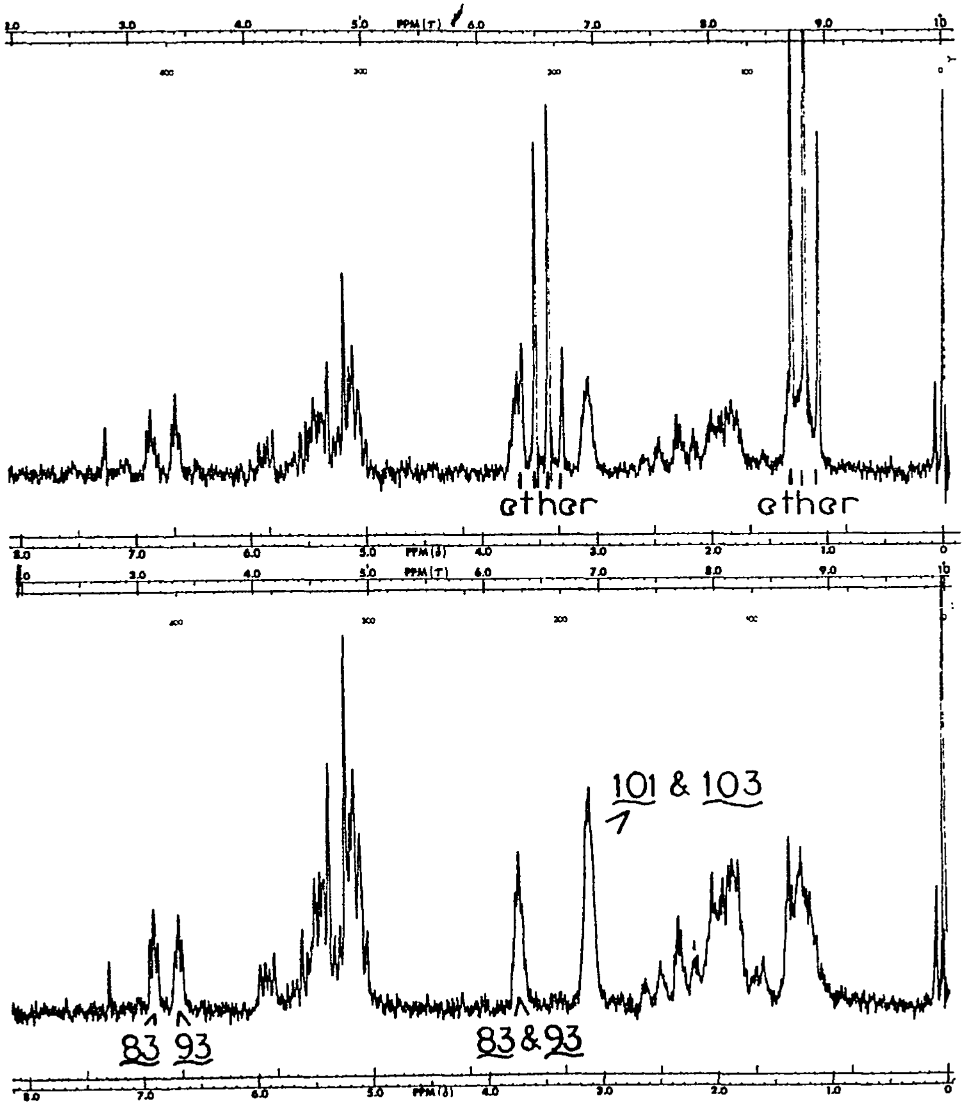
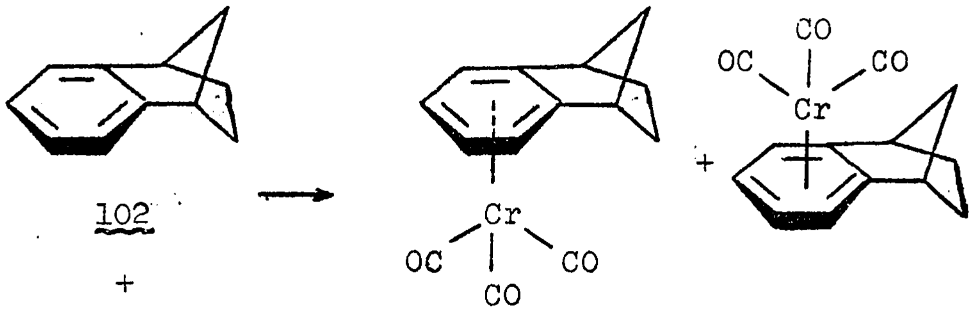

2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0
ether
ether
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0
101 & 103
83
93
83 & 93

Table 34. Relative rate constants for hydrogenation of free benzonorbornadiene and its tricarbonylchromium complexes.

Olefin	Relative rate constant
Free (**81**)	7.2
Syn complex (**83**)	1.0
Anti complex (**93**)	3.0

determination of the relative stabilities of all species involved (this will be amplified upon later).

Comparison of the nmr of the complexed products (Figure 43) with those of the pure *anti*- and *syn*-complexes shows that, if the complexation of benzonorbornene is product controlled, the *syn*-complex, **101**, is 1.32 kcal/mole



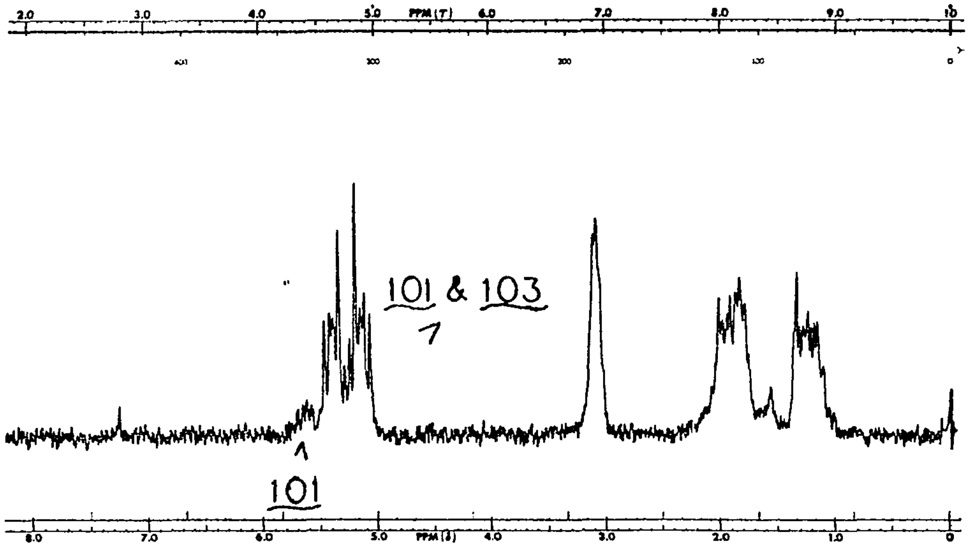
102 + $(MeCN)_3Cr(CO)_3$ → **101** + **103**

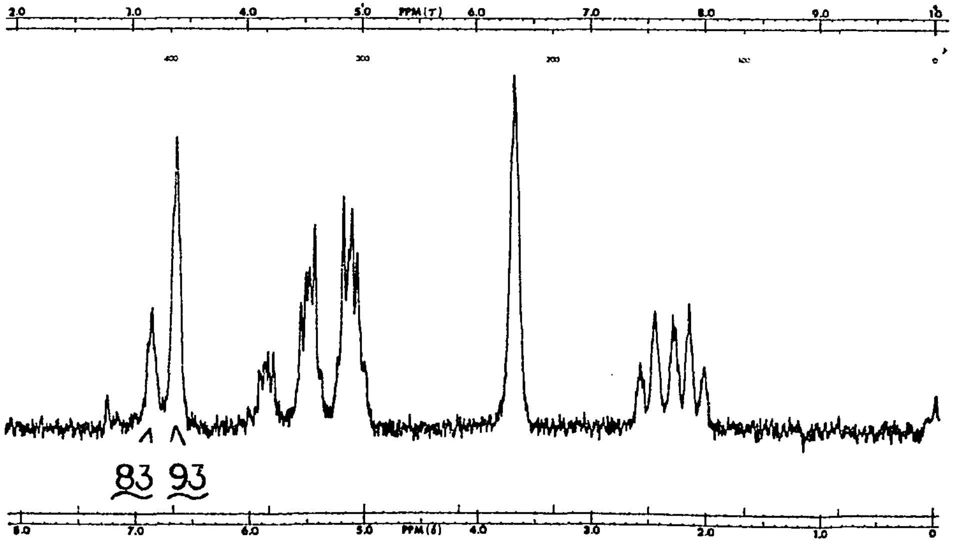
1:6

(48)

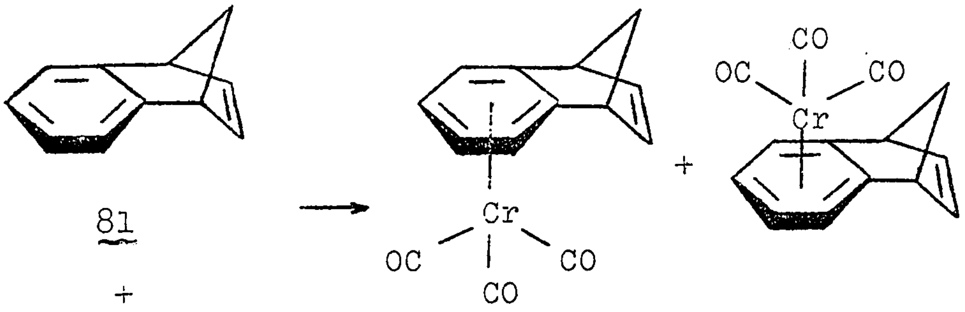
Figure 43. A-60 nmr spectrum, in deuterochloroform, of product of complexation of benzonorbornene

Figure 44. A-60 nmr spectrum, in deuterochloroform, of product of complexation of benzonorbornadiene


2.0 3.0 4.0 5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
400 300 200 100 0
101 & 103
101
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0


2.0 3.0 4.0 5.0 PPM (τ) 6.0 7.0 8.0 9.0 10
400 300 200 100 0
83 93
8.0 7.0 6.0 5.0 PPM (δ) 4.0 3.0 2.0 1.0 0

more unstable than the *anti*-isomer, 103. There is the legitimate question of whether thermodynamic control is indeed involved. The complexation of benzonorbornadiene, 81, can demonstrate initial kinetic control; when the reaction is carried out for 10 minutes or less, there is



81 + $(MeCN)_3Cr(CO)_3$ → 83 + 93 (49)

33:71

easily isolated pure *syn*-complex, 83. If the reaction is allowed to proceed longer, the appearance of the *anti*-isomer, 93, inhibits isolation of pure complex and after 30 minutes, from examination of the nmr spectrum of the product mixture, the ratio of *anti*- to *syn*-complex stabilizes at about 2 to 1. Because the ethano bridge probably responsible for the kinetic favoring of the *syn*-isomer does not exist in reaction with benzonorbornene (Equation 48), thermodynamic control presumably persists throughout the entire reaction time. Nevertheless, this matter should be pursued further. Chart 2 interrelates all rate and thermodynamic data accumulated.

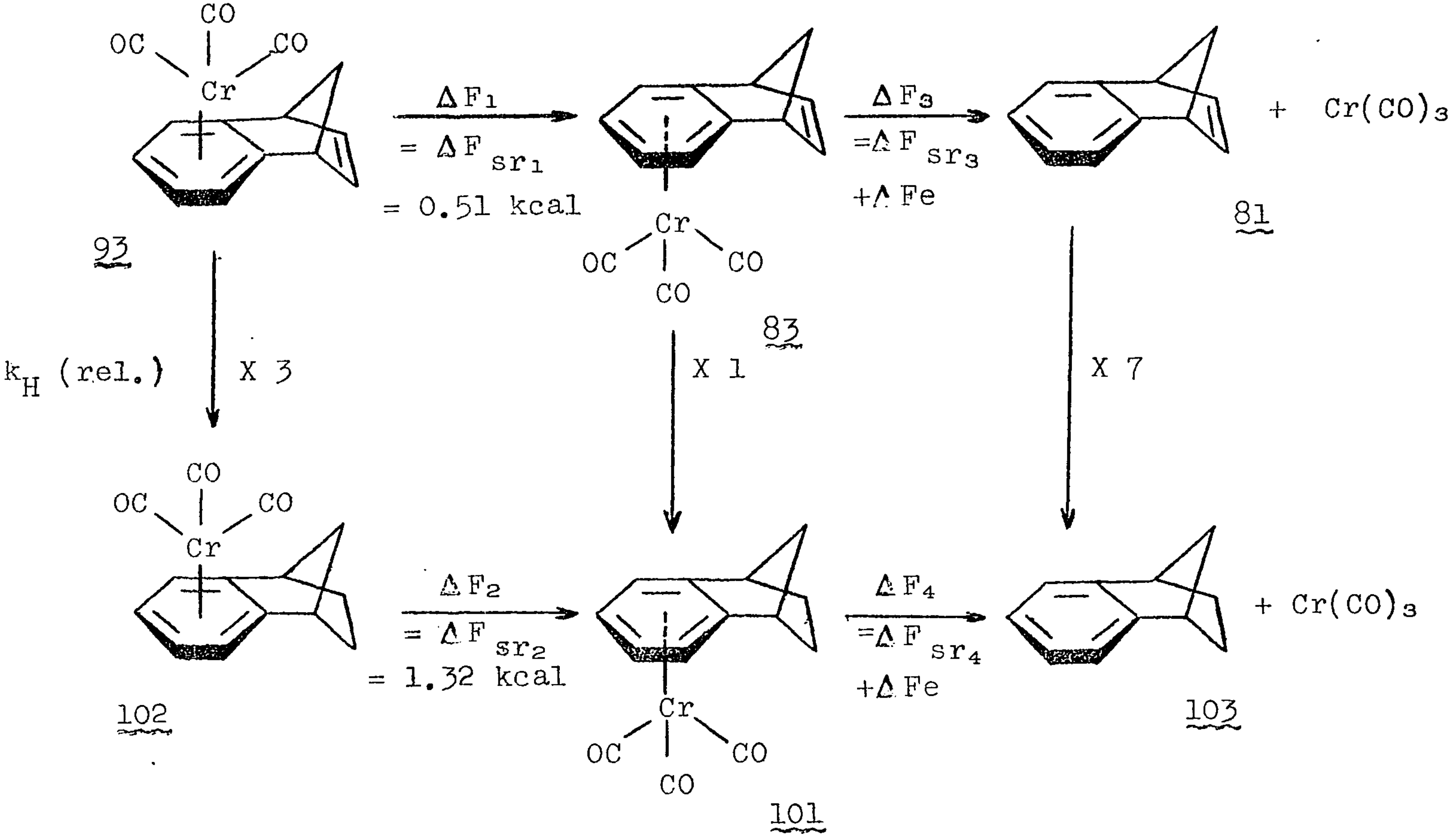


Chart 2. Relationship of kinetic and thermodynamic data

The relative rate of hydrogenation of anti- and syn-complexed olefins is 3:1. Thus the difference in activation free energy for these species is,

$$2.3\ RT\ \log(k_{\underline{anti}}/k_{\underline{syn}}) = 0.65\ \text{kcal} \qquad (50)$$

This nearly equals the difference in the two free energies of isomerization (0.81 kcal/mole). It appears then that the relative rates of hydrogenation may be an accurate estimate of the differences in the isomerization free energies. If this is so, then the difference in the energies of decomplexation of the syn olefin, 83, and syn saturate, 101, are given by,

$$2.3\ RT\ \log k = 1.2\ \text{kcal} \qquad (51)$$

The free energies of decomplexation are sums of the respective steric and electronic free energies,

$$\Delta F = \Delta F_{sr} + \Delta F_{e} \qquad (52)$$

but the electronic energies should be very nearly the same. Therefore, the difference in the steric relief energies upon decomplexation is 1.2 kcal. In other words, steric relief energy on conversion of syn saturate, 101, to syn olefin, 83, is 1.1 kcal greater than that for conversion of benzonorbornene to benzonorbornadiene. The additional steric strain in the *syn* saturate, **101**, amounts to a rate enhancement of 3 fold at 80°.

This value is clearly not nearly sufficient to account for the 280 fold rate enhancement of *syn*-(benzonorbornen-2-(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium over the *anti*-isomer. We favor the interpretation of the "non-steric" acceleration to be the operation of the "σ-d" mechanism. The (phenyl)tricarbonylchromium operates as a "neighboring group" and the ferrocenyl group, which is isoelectronic, is a "hyperconjugative group."

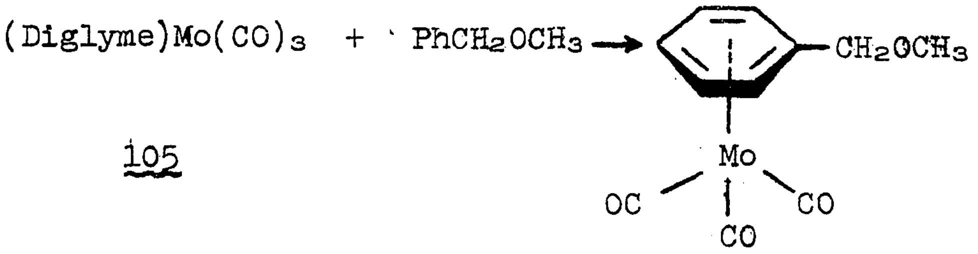
(Arene)tricarbonyl Complexes with Molybdenum(0) and Tungsten(0)

A natural extension of our work on the tricarbonylchromium complexes of benzyl systems would be the observation of the effects of moving down group VI-B, through molybdenum and tungsten. In particular, if this group trended similarly to group V-B (15), the pK_{R^+} of the (benzyl)tricarbonylmolybdenum and (benzyl)tricarbonyltungsten cations should be larger (more stable) than the pK_{R^+} for the (benzyl)tricarbonylchromium cation.

Tricarbonylmolybdenum

The first (arene)tricarbonylmolybdenum complex was prepared by Fischer and Öfele (68) in 1958. These complexes have since been shown to be thermally labile compared to the analogous chromium complexes (69), and no chemistry has been performed upon the complexed arene, aside from exchange reactions (70).

The preparation of (benzyl methyl ether)tricarbonylmolybdenum, 104, the first tricarbonylmolybdenum complex involving a hetero atom β to the aromatic system (these are electron deprived systems), went smoothly if precautions against air oxidation during reaction with (diglyme)tricarbonylmolybdenum, 105, were taken.



(53)

105

104

The injection of an ethanolic solution of the complex, 104, into sulfuric acid-water produced no change in the absorption spectrum (Table 35).

Treatment of a benzene solution of 104 with concentrated hydrochloric acid gave immediate decomposition; the reddish color produced could be pulled off into the water layer, and was probably a molybdenum ion of some kind.

Table 35. Spectra of (benzyl methyl ether)tricarbonylmolybdenum and tricarbonyltungsten in ethanol and sulfuric acid

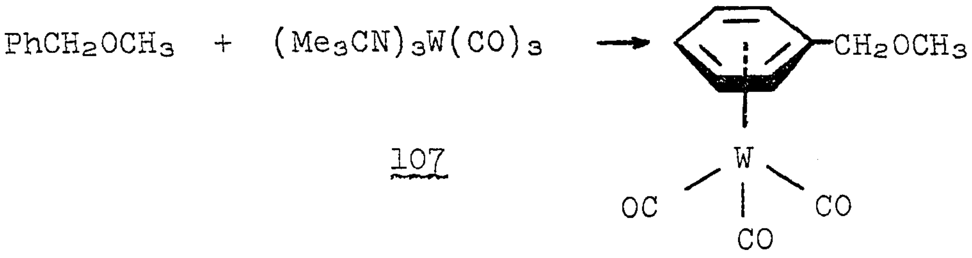
Complexed metal	95% EtOH	61.0% H_2SO_4	77.5% H_2SO_4	94.2% H_2SO_4
Mo	2600 (1230) 3100 (660) 4000 (160)	2580 (485) 3100 (580) 4000 (?)		2600 (1070) 3200 (980) 4000 (195)
W	2060 (19800) 3160 (18900) 3590 (1130)		4800 (383) --[a]	

[a] Because of rapid decomposition, it was difficult to obtain uv spectrum.

Tricarbonyltungsten

The first preparation of an (arene)tricarbonyltungsten complex was that of Fischer and Öfele (68) in 1958. No chemistry has been performed upon the organic ligand aside from exchange reactions (70).

Preparation of (benzyl methyl ether)tricarbonyltungsten, **106**, the first (arene)tricarbonyltungsten containing an hetero atom β to the arene, was effected through treatment of (triacetonitrile)tricarbonyltungsten (71), **107**, with benzyl methyl ether. This complex was about as air stable as a typical tricarbonylchromium complex.



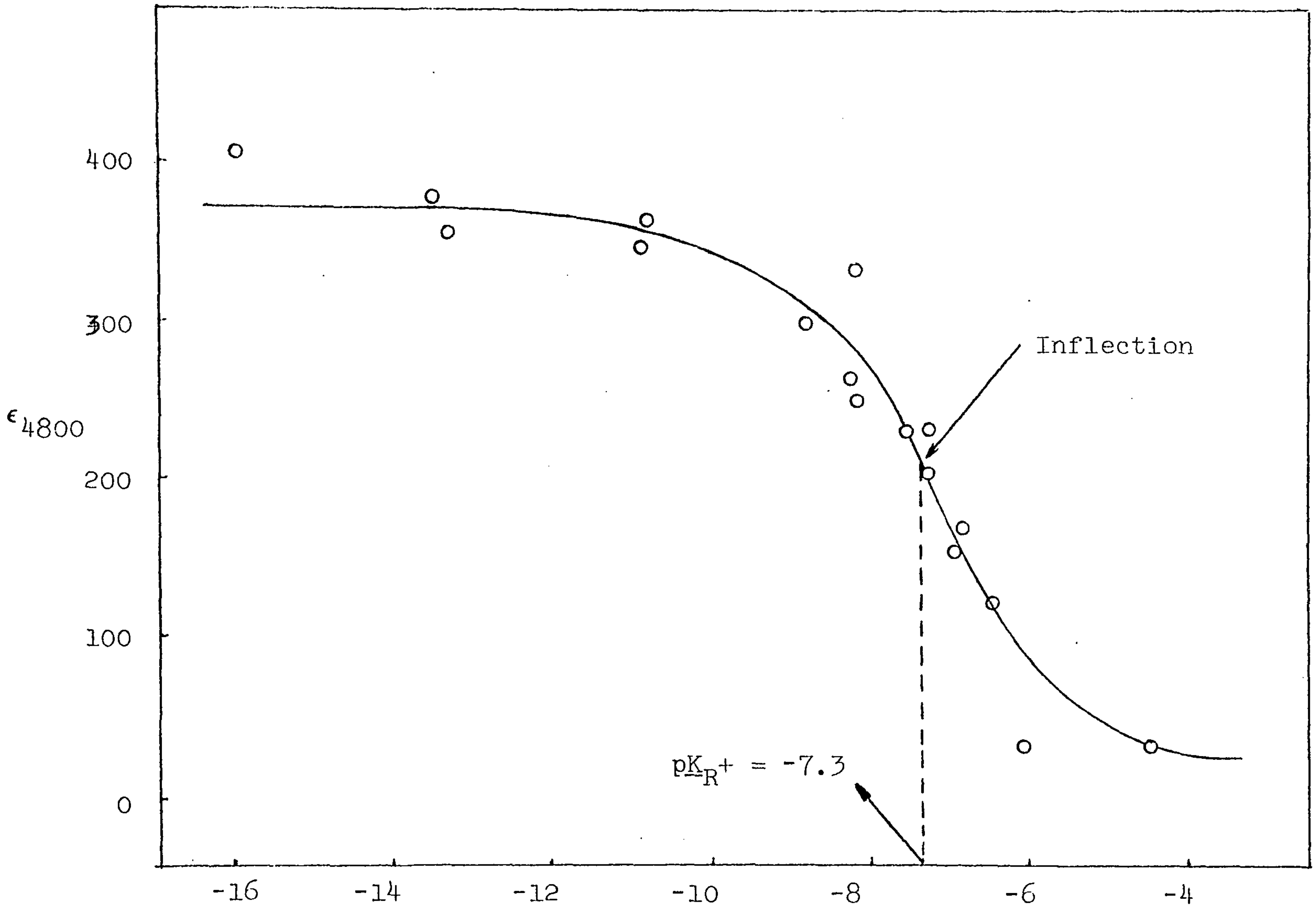
(54)

107

106

Injection of an acetic acid solution into aqueous sulfuric acid gave rise to a spectral change (Table 35). The plot of ϵ *vs*. C_o gave an inflection corresponding to $pK_{R^+} = -7.3$ (Figure 45); this compares with a pK_{R^+} of < -17.3 for the benzyl cation and -11.8 for the (benzyl)tricarbonylchromium cation. To confirm the apparent high stability of the (benzyl)tricarbonyltungsten cation, an attempted preparation of (benzyl chloride)tricarbonyltungsten, which would have been subjected to solvolysis, was carried out by treating the ether, 106, with concentrated hydrochloric acid. At moderate speed, the color of the organic layer turned dark; vigorous shaking put the colored specie, probably a tungsten ion, in the aqueous layer. The organic layer was still yellow, and the workup (see Experimental) gave a yellow oil which was very heat sensitive. If this makes for a stable cation ($pK_{R^+} = -7.3$), then it may also

Figure 45. The molar extinction coefficient of (benzyl)tricarbonyltungsten cation at 4800 Å _vs._ the C_o of the sulfuric acid-water solvent



400
300
200
100
0
ε4800
-16
-14
-12
-10
-8
-6
-4
Inflection
pK_R+ = -7.3

readily displace the chloride, either intra- or intermolecularly, giving an oxidized tungsten specie. Further work in this area is justified.

CHAPTER IV. EXPERIMENTAL

Equipment

The apparatus used in performing all complexations was constructed according to the instructions of Strohmeier (72).

A Beckman IR 12 Infrared Spectrophotometer was used to obtain carbonyl stretching frequencies; routine spectra were obtained on the Perkin-Elmer 21 Infrared Spectrophotometer.

The ultra-violet and visible spectra were taken on a Cary 14 Spectrophotometer.

Nuclear magnetic spectra were run on a Varian A-60b Nuclear Magnetic Resonance Spectrometer; variable temperature work employed the V-6057 variable temperature system which involved the V-6031 variable temperature probe.

The temperatures of solvolytic baths were maintained by Fischer Proportional Temperature Control Unit, No. 15-177-50.

Titrations of acid in the solvolysis runs utilized an automatic 10 ml burette, graduated in 1/50 ml, Kimax-17115.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus.

One of the benzamides was collected on the Aerograph 200 Gas-Liquid Phase Chromatograph.

Commercial Compounds

Table 36. Source of commercial compounds

Compound	Source
Acetonitrile	Mallinckrodt
Benzene	Mallinckrodt
Pentane	Mallinckrodt
Ethyl ether	Mallinckrodt
Chloroform	Mallinckrodt
Pyridine	Baker
Dioxane	Baker
Acetone	Mallinckrodt
Methanol	Baker
Toluene	Baker
Glyme	Aldrich
Diglyme	Aldrich
Butyl ether	Eastman
Acetophenone	Matheson, Coleman, and Bell
Benzaldehyde	Baker
Benzophenone	Fisher

Table 36 (Cont.)

Compound	Source
Benzoic acid	Mallinckrodt
Benzyl alcohol	Baker
Methylene chloride	Mallinckrodt
Thionyl chloride	Baker and Fisher
Hydrochloric acid	Mallinckrodt
Sulfuric acid	Baker
Diphenylmethanol	Matheson, Coleman, and Bell
Benzyl chloride	Baker
Tetrahydrofuran	Baker
n-Butyllithium	Foote
Lithium Aluminum Hydride	Ventron
Sodium Borohydride	Ventron
t-Butyl chloride	Baker
Dimethylamine	City Products
Hexacarbonylchromium	Strem
Hexacarbonylmolybdenum	Strem
Hexacarbonyltungsten	Strem
p-Methylbenzyl alcohol	Aldrich
p-Methoxybenzyl alcohol	Aldrich
p-Chlorobenzyl alcohol	Aldrich
p-*t*-Butylbenzoic acid	Aldrich
3,5-Di-methylbenzoic acid	Aldrich

Table 36 (Cont.)

Compound	Source
p-Isopropylbenzoic acid	Eastman
p-Methylbenzoic acid	Matheson, Coleman, and Bell
p-Methoxybenzoic acid	Matheson, Coleman, and Bell
p-Fluorbenzoic acid	Aldrich
p-Benzoquinone	Matheson, Coleman, and Bell
2,4,6-Trimethylbenzoic acid	Aldrich
Deuterium oxide	Columbia
10% Palladium on charcoal	Matheson, Coleman, and Bell
Triethyl orthoformate	Aldrich
4-Biphenylcarboxylic acid	Aldrich
p-Nitrobenzoyl chloride	Matheson, Coleman, and Bell
p-Cyanobenzoic acid	Aldrich
N,N-dimethylbenzamide	Eastman
Methyl benzoate	Matheson, Coleman, and Bell
Deuterochloroform	Columbia
p-Methoxydiphenyl ketone	Aldrich
Dicyclopentadiene	Eastman
Bromobenzenesulfonyl chloride	Eastman
Bromothymol blue	Baker

Prepared Compounds

All melting points are uncorrected.

Analyses of new compounds were carried out by the Spang Microanalytical Laboratory (Ann Arbor, Michigan) and the Ilse Beetz Microanalytical Laboratory (Germany).

(Triacetonitrile)tricarbonylchromium (82)

Prepared according to the procedure of King (71).

Into a 50 ml round bottom flask, equipped with a sidearm stopcock, was placed about 2 g hexacarbonylchromium, about 15 ml acetonitrile, and a boiling chip. The flask was attached to the Strohmeier apparatus, the stopcock was opened, and a nitrogen stream was passed through the apparatus for about 10 minutes. Finally the rate of passage of the nitrogen was slowed, access to the bubbler was established, the stopcock was closed, and the apparatus was lowered until the level of the acetonitrile was about 5 mm above the level of the silicon oil in an oil bath. The hot plate was turned to "4.5" or "5." Cold tap water was passed through the top two condensers, and hot tap water which was subsequently passed slowly through a 75° oil bath was fed into the bottom condenser. As the acetonitrile refluxed, hexacarbonyl sublimed onto the walls surrounded by the middle condenser jacket; the bottom trap was eventually filled with acetonitrile, and the reaction flask was lowered or raised until the level of the acetonitrile was just above the level of the oil in the oil bath. After the sublimed hexacarbonyl established a constant amount on the walls, the passage of cold water through the middle jacket was discontinued, and hot tap water (*ca.* 55°) was fed into it. In about one day, the hexacarbonyl disappeared and refluxing was continued (usually about one more day) until no hexacarbonyl could be condensed onto the walls within the middle jacket when it was fed by cold water. At this time, the entire apparatus was bodily removed from its clamps, and the acetonitrile was shaken out of the bottom trap into the reaction flask; the apparatus was quickly re-clamped, nitrogen stream was increased, the stopcock on the reaction flask was opened, and the apparatus was lowered so that the reaction flask was barely touching the hot oil bath. All the acetonitrile was thus blown out, and the passage of the stream was continued thereafter for about 5 minutes, with the reaction flask well out of the way of the oil bath, to ensure that traces of acetonitrile were removed. Finally, the nitrogen stream was reduced, the stopcock was closed, and the yellow-orange contents, (triacetonitrile)tricarbonylchromium, were ready for treatment with dioxane solutions of appropriate arenes desired to be complexed.

(Benzene)tricarbonylchromium (**1**)

Prepared according to a modification of the procedures of Nicholls and Whiting (13).

The (triacetonitrile)tricarbonylchromium from 3.79 g hexacarbonylchromium was refluxed in 20 ml benzene overnight, under nitrogen, in the Strohmeier apparatus. Filtration of the cooled reaction mixture through a Celite bed with suction and removal of the solvent gave 2.257 g (61%), mp 158-162° (dec), lit. (13) mp 165.5-166.5.

(Benzyl alcohol)tricarbonylchromium (**17**)

Prepared according to a modification of the procedure of Nicholls and Whiting (13).

A mixture of 7 ml benzyl alcohol and the (triacetonitrile)tricarbonylchromium from 6.274 g hexacarbonylchromium was refluxed 1/2 hour under nitrogen in the Strohmeier apparatus. The cooled reaction mixture was taken up in ether, filtered through Celite, and the filtrate was washed with water. The ethereal portion was dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. The yellow oil was swirled in a mixture of 10% ether-pentane, whereupon crystallization began. After standing in ice box, 1.71 g crystals could be collected, mp 92.5-94°, lit. (13) mp 95.5-96.5°.

(p-Methylbenzyl alcohol)tricarbonylchromium (18)

A mixture of 3.2 g p-methylbenzyl alcohol and 3.2 g (triacetonitrile)tricarbonylchromium was refluxed in the Strohmeier apparatus under nitrogen for 50 minutes in 15 ml dry dioxane. The cooled reaction mixture was filtered through a Celite bed with suction and with ether rinses. The filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. When the resultant oil was swirled in 30 ml hexane, crystallization ensued. The crystals were titrated with several hexane portions, and recrystallized (hexane-ether, methylene chloride-pet ether), to yield 2.57 g (68%), mp 80.5-81.5°; nmr ($CDCl_3$) δ 5.3 (AA'BB' pattern, m, J_{AB} = 6 Hz), 4.37 (s (broad), 2), 2.18 (s, 3), and 1.87 ppm (s (very broad), 1); nmr ($CDCl_3$-D_2O) δ 5.3 (AA'BB' pattern, m, J_{AB} = 6 Hz), 4.37 (s (sharp), 2), and 2.18 ppm (s, 3).

Anal. Calcd. for $C_{11}H_{10}CrO_4$: C, 51.17; H, 3.90. Found: C, 51.68; H, 3.90.

(p-Methoxybenzyl alcohol)tricarbonylchromium (19)

A mixture of 4 ml p-methoxybenzyl alcohol was refluxed with the (triacetonitrile)tricarbonylchromium from 2.748 g hexacarbonylchromium in 11 ml dry dioxane under nitrogen in the Strohmeier apparatus for 45 minutes. The cooled reaction mixture was filtered through a Celite bed with suction and with ether rinses and the ethereal filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent was removed to give an oil. Chromatography on silica gel gave the complex (benzene), and upon removing the solvent with the rotary evaporator and then placing the resulting oil in the ice box, crystallization ensued. Recrystallizations (ether-hexane, methylene chloride-pentane) gave mp 60.0-61.8°; nmr ($CDCl_3$) δ 5.40 (AA'BB' pattern, 4, $\underline{J}_{AB}$ = 7 Hz), 4.30 (s (broad), 2), 3.70 (s, 3) and 1.83 ppm (s, 1).

Anal. Calcd. for $C_{11}H_{10}CrO_5$: C, 48.18; H, 3.68. Found: C, 48.54; H, 3.75.

(p-Chlorobenzyl alcohol)tricarbonylchromium (20)

A mixture of 3.03 g p-chlorobenzyl alcohol and the (triacetonitrile)tricarbonylchromium from 1.83 g hexacarbonylchromium was refluxed 5 hours, under nitrogen, in the Strohmeier apparatus, in 13 ml dry dioxane. The cooled reaction mixture was filtered through a Celite bed with suction and with ether rinses, and the ethereal filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent removed on the rotary evaporator to give a solid which was chromatographed on silica gel. The third band was collected (1:1 chloroform-benzene), the solvent was removed on the rotary evaporator and the hexacarbonylchromium present was sublimed out. The remaining yellow solid was sublimed (80^{o}/0.01 mm) to give 89.5 mg (3.9%), mp 88-89° (methylene chloride-pentane); ir (KBr) 1960, 1900, 1880, and 1850 cm^{-1} (-C=O).

Anal. Calcd. for $C_{10}H_{7}ClCrO_{4}$: C, 43.11; H, 2.43. Found: C, 43.26; H, 2.48.

p-t-Butylbenzyl alcohol

Prepared by the esterification of p-t-butylbenzoic acid and subsequent reduction with lithium aluminum hydride; nmr (CCl_4) δ 7.2 (AA'BB' pattern, 4, J_{AB} = 2-4 Hz), 4.7 (s, 2), 1.8 (s, 1), 1.3 (s, 9) and 3.3 ppm (0.7, impurity).

(p-t-Butylbenzyl alcohol)tricarbonylchromium

A mixture of the (triacetonitrile)tricarbonylchromium from 2.493 g hexacarbonylchromium and 3.44 g p-t-butylbenzyl alcohol was refluxed 85 minutes in 20 ml dry dioxane, under nitrogen, in the Strohmeier apparatus. The cooled reaction mixture was taken up in ether, filtered through a Celite bed with suction, and the solvent was removed on the rotary evaporator to give an orange-green oil. The oil was taken up in ether and washed with dilute hydrochloric acid, dilute sodium bicarbonate, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. Pentane was swirled over the yellow oil and the crystals which formed were washed with pentane, 1.457 g (40%), mp 98.5-100.5; then mp 100.4-101.8 (ether-hexane, methylene chloride-hexane); nmr ($CDCl_3$) δ 5.4 (AA'BB' pattern, 4, J_{AB} = 7-10 Hz), 4.5 (s (broad), 2), and 1.3 ppm (s, 9); nmr ($CDCl_3$-D_2O) 5.4 (AA'BB' pattern, 4, J_{AB} = 7-10 Hz), and 4.5 ppm (s (sharp), 2).

Anal. Calcd. for $C_{14}H_{16}CrO_4$: C, 56.00; H, 5.37. Found: C, 55.97; H, 5.36.

3,5-Di-*t*-butyltoluene

Prepared according to the procedure of Gruze *et al.* (73), bp 107-116°/13 mm, lit. (73) bp 98°/5.7 mm; nmr (CCl_4) δ 7.1 (t, 1), 6.9 (m, 2), 2.3 (s, 3), and 1.29 ppm (s, 18).

3,5-Di-*t*-butylbenzoic acid

Prepared according to the procedure of Hartingsveldt *et al.* (74), from 3,5-di-*t*-butyltoluene, mp 167-170°, lit. (74) mp 171.5-172.5°.

3,5-di-*t*-butylbenzyl alcohol

To a stirring mixture of 0.859 g lithium aluminum hydride in 100 ml ether was added a solution of 5.234 g 3,5-di-*t*-butylbenzoic acid. After the addition was complete, stirring was continued for 3 hours. The excess hydride was destroyed with excess water and dilute hydrochloric acid and the mixture was stirred until the aqueous and ethereal layers were clear. The aqueous layer was separated and extracted with 100 ml ether. The combined ether portions were washed with water, dilute sodium bicarbonate solution, water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. The residue crystallized from hexane, while standing in ice box; nmr (CCl_4) δ 7.2 (m, 1), 7.1 (m, 2), 4.8 (s, 2), 1.5 (s (broad), 1), and 1.3 ppm (s, 18).

(3,5-Di-*t*-butylbenzyl alcohol)tricarbonylchromium

A mixture of the (triacetonitrile)tricarbonylchromium from 1.837 g hexacarbonylchromium and 4.13 g crude 3,5-di-*t*-butylbenzyl alcohol was refluxed in 20 ml dioxane, under nitrogen, in the Strohmeier apparatus, for 90 minutes. The cooled reaction mixture was taken up in ether and filtered through a Celite bed with suction. The solvent was removed from the filtrate and the addition of pentane to the yellow oil gave crystals. These were collected and washed with pentane, 2.00 g (68%), mp 125-127°; nmr ($CDCl_3$) δ 5.7 (s, 3), 4.4 (s, 2), 1.6 (s, (very broad), 1) and 1.3 ppm (s, 18); nmr ($CDCl_3$-D_2O) δ 5.7 (s, 3), 4.4 (s, 2) and 1.3 ppm (s, 18).

Anal. Calcd. for $C_{18}H_{24}CrO_4$: C, 60.66; H, 6.79. Found: C, 60.82; H, 6.71.

2,4,6-Trimethylbenzyl alcohol

Prepared by esterification of mesitoic acid and lithium aluminum hydride reduction of the ester; mp 85.8-87.4°, lit. (75) mp 88-89°.

(2,4,6-Trimethylbenzyl alcohol)tricarbonylchromium

A mixture of 2.311 g of 2,4,6-trimethylbenzyl alcohol and the (triacetonitrile)tricarbonylchromium from 2.188 g hexacarbonylchromium was refluxed 1/2 hour, under nitrogen, in the Strohmeier apparatus, in 20 ml dioxane. The cooled reaction mixture was filtered through a bed of Celite with suction and with ether rinses. The filtrate was washed thoroughly with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. This yellow oil was swirled in pentane several times (crystallization), discarding the yellow pentane solution each time. The yellow residue was recrystallized from methylene chloride-hexane to give prisms, and after cooling to 0° to obtain more crystals, obtained mp ~85°. Elution off of silica gel (benzene) gave yellow solid, 0.521 g, mp 101.4-103.4° (methylene chloride-hexane); nmr ($CDCl_3$) δ 4.9 (s, 2), 4.6 (s, 2), 2.4 (s, 6), 2.2 (s, 3), and 1.5 ppm (s (very broad), 1); nmr ($CDCl_3$-D_2O) δ 4.9 (s, 2), 4.6 (s, 2), 2.4 (s, 6) and 2.2 ppm (s, 3); mp 102.5-104.5° (methylene chloride-pentane).

Anal. Calcd. for $C_{13}H_{14}CrO_4$: C, 54.54; H, 4.93. Found: C, 54.31; H, 4.87.

3,5-Di-methylbenzyl alcohol

Treatment of 3,5-di-methylbenzoic acid with thionyl chloride-methanol-lithium aluminum hydride gave the alcohol, in a 3:1 mixture with the methyl ester (the reduction was incomplete). This mixture was submitted to complexation (below).

(3,5-Di-methylbenzyl alcohol)tricarbonylchromium

A mixture of 4 ml of a 3:1 mixture of 3,5-di-methylbenzyl alcohol and its methyl ester (the mixture was a result of incomplete lithium aluminum hydride reduction of the methyl ester) and the (triacetonitrile)tricarbonylchromium from 2.28 g hexacarbonylchromium was refluxed in 13 ml dry dioxane, under nitrogen, in the Strohmeier apparatus, for 45 minutes. The cooled reaction mixture was taken up in ether, filtered through a Celite bed with suction, washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator to give a yellow mass, 0.905 g (29%), mp 131.4-133.2° (methylene chloride-hexane); sublimation: mp 131.8-132.8°; nmr ($CDCl_3$) δ 5.0 (m, 3), 4.5 (s (broad), 2), 2.22 (s, 6) and 2.00 ppm (s (very broad), 1); nmr ($CDCl_3$-D_2O) δ 5.10 (m, 3), 4.5 (s (sharp), 2), and 2.22 ppm (s, 6).

Anal. Calcd. for $C_{12}H_{12}CrO_4$: C, 52.94; H, 4.44. Found: C, 53.31; H, 4.43.

p-Isopropyl N,N-dimethylbenzamide

p-Isopropylbenzoic acid was converted to the acid chloride with thionyl chloride; subsequent treatment with dimethylamine gave the amide, bp 93-97°/0.01 mm, mp ~25°; nmr ($CDCl_3$) δ 7.30 (AA'BB' pattern, 4, J_{AB} = 3-7 Hz), 3.08 (s, 6), 1.2 (d, 6, J = 7 Hz) and 2-3 ppm (m, 1).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.22; H, 8.98; N, 7.58.

p-Methyl N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment upon p-toluic acid, mp 81.5-82.8°/0.01 mm, mp 38-41°, lit. (76) bp 156°/10 mm, lit. (76), mp 41°; nmr ($CDCl_3$) δ 7.24 (AA'BB' pattern, 4, J = 5-9 Hz), 3.03 (s, 6), and 2.36 ppm (s, 3).

p-t-Butyl N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment upon p-t-butylbenzoic acid, mp 86-87° (hexane); nmr ($CDCl_3$) δ 7.4 (s, 4), 3.08 (s, 6), and 1.35 ppm (s, 9).

p-Methoxy N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment upon anisic acid, bp 120-122°/0.03 mm, mp 37.5-40.3°, lit. (77) bp 196°/16 mm; nmr ($CDCl_3$) δ 6.8-7.6 (AA'BB' pattern, 4, J = 8 Hz), 3.8 (s, 3), 3.0 (s, 6), and 1.9 ppm (0.5, impurity).

p-Fluoro N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment on p-fluorobenzoic acid, bp 76.7-87°/<0.01 mm; the distillate crystallized on standing in ice box, mp 65-67.3° (hexane); nmr ($CDCl_3$) δ 7.3 (m, 4) and 3.08 ppm (6, s).

Anal. Calcd. for $C_9H_{10}FNO$: C, 64.66; H, 6.03. Found: C, 64.63; H, 6.00.

p-Chloro N,N-dimethylbenzamide

Used as obtained from Dr. Norman Heimer, mp 57-60.5°, lit. (78) mp 55-59°; nmr ($CDCl_3$) δ 7.4 (s, 4) and 3.05 ppm (s, 6).

p-Bromo N,N-dimethylbenzamide

Used as obtained from Dr. Norman Heimer, mp 69-71.5°, lit. (79) mp 72°; nmr ($CDCl_3$) δ 7.4 (AA'BB' pattern, 4, J_{AB} = 5-9 Hz) and 3.05 ppm (s, 6).

p-Phenyl N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment upon 4-biphenylcarboxylic acid, mp 104.5-105.5, lit. (80) mp 105.5-106.5°; nmr ($CDCl_3$) δ 7.2-7.7 (m, 9) and 3.1 ppm (s, 6).

p-Amino N,N-dimethylbenzamide

Used as obtained from Dr. Norman Heimer, mp 145-153°, lit. (81) mp 152-153°; nmr ($CDCl_3$) δ 6.5-7.4 (AA'BB', 4, J_{AB} = 8 Hz), 3.8 (s (broad), 2), and 3.0 ppm (s, 6).

p-Nitro N,N-dimethylbenzamide (43)

Prepared by treatment of p-nitrobenzoyl chloride with dimethylamine, mp 97-98.5°, lit. (82) mp 97°; nmr ($CDCl_3$) δ 7.8 (AA'BB' pattern, 4) and 3.02 ppm (s, 6).

p-Cyano N,N-dimethylbenzamide

Prepared by the thionyl chloride-dimethylamine treatment upon p-cyanobenzoic acid, mp 93.7-95.6°; nmr ($CDCl_3$) δ 7.7 (AA'BB' pattern, 4, J_{AB} = 4-8 Hz) and 3.07 ppm (s, 6).

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79. Found: C, 68.35; H, 5.78.

3-Dimethylaminovinyl phenyl ketone (44)

Prepared according to the procedure of Pasteur *et al.* (83), mp 89.3-91.3°, lit. (83) mp 88-89°; nmr ($CDCl_3$) δ 7.2-8.0 (m, 6), 5.67 (d, 1, J = 13 Hz) and 3.0 ppm (s, 6).

(N,N-dimethylbenzamide)tricarbonylchromium (42)

N,N-dimethylbenzamide, 2 ml, 1.969 g hexacarbonylchromium, 2 ml diglyme, and 6 ml glyme was saturated with nitrogen and then refluxed under nitrogen in the Strohmeier apparatus for 11.5 hours. Hexane was added at time to time to maintain refluxing of solvent down through the condenser. The reaction mixture was allowed to cool, diluted with 5 ml ether, and filtered through a Celite bed with suction. The orange-yellow filtrate was washed with nitrogen-saturated water several times, dried ($MgSO_4$), and filtered. The solvent was removed on the rotary evaporator with water aspirator vacuum and then an oil pump vacuum. The orange oil was taken up in ether and filtered through a Celite bed with suction. The solvent was removed from the filtrate with the rotary evaporator to give a mixture of oil and crystals. To this residue was added 4 ml of 3:1 hexane-ether and it was allowed to stand; the resulting crystals were rinsed onto a sintered glass funnel, washed with two portions of 4 ml 1:1 hexane-ether and one 5 ml portion of 3:2 ether-hexane, and dried in vacuo, to give 0.474 g (19%), mp 95.4-96.7°, mp 96.0-97.7° (methylene chloride-pentane); ir ($CHCl_3$) 1630, 1905, and 1975 cm^{-1}; nmr ($CDCl_3$) δ 5.45 (m, 5) and 3.10 ppm (s, 6).

Anal. Calcd. for $C_{12}H_{11}CrNO_4$: C, 50.53; H, 3.89. Found: C, 50.74; H, 3.93.

(3-Dimethylaminovinyl phenyl ketone)tricarbonylchromium (45)

To a mixture of 0.219 g of sodium methoxide stirring in 2 ml ether was added a solution of 0.945 g (acetophenone)-tricarbonylchromium and 0.301 g ethyl formate in 11 ml ether drop by drop. After the addition was finished, 0.1 ml ethyl formate and about 0.05 g sodium methoxide was added, and the reaction mixture was allowed to stir a few hours to complete the precipitation. Finally, the reaction mixture was transferred to a separatory funnel using water, dilute hydrochloric acid, and ether rinses as needed, and shaken. The red ether layer was separated and the orange aqueous layer was extracted with ether several times. The combined ethereal extracts were washed with 3 x 20 ml water, dried ($MgSO_4$) and filtered. The filtrate was evaporated to about 40 ml on the rotary evaporator, a little anhydrous sodium sulfate added, and the mixture was stirred in an ice bath while excess ethereal dimethylamine was added. The reaction mixture was taken down to dryness on the rotary evaporator, the residue was taken up in hot benzene, filtered, and boiled down, with addition, at time to time, of hexane. At about 50 ml, the hot solution was allowed to cool. The resulting crystals were washed with cold 1:1 hexane-benzene, 0.455 g, mp 179° (dec); mp 183-185° (methylene chloride-pentane); nmr ($CDCl_3$) δ 7.82 (m, 1), 6.06 (m, 1), 5.2-5.8 (m, 5), and 3.03 ppm (s, 6); mass spectrum *m/e* 311.

Anal. Calcd. for $C_{14}H_{13}CrNO_4$: C, 54.00; H, 4.21; N, 4.50. Found: C, 53.91; H, 4.13; N, 4.69.

Benzaldehyde diethyl acetal

Prepared by the procedure of Claisen (84), bp 217-223°, lit. (84) bp 217-223°.

(Benzaldehyde)tricarbonylchromium (**36**)

Prepared according to the procedure of Drefahl *et. al*. (85), mp 79.5°, lit. (85) mp 78.5-79.5°.

Acetophenone, diethyl ketal

Prepared according to the procedure of Fuson and Burness (86), bp 104.0-107.0°/17 mm, lit. (86) bp 101.5°/ 17 mm.

(α-Ethoxystyrene)tricarbonylchromium

A mixture of 3.01 g hexacarbonylchromium, 7 ml diethyl ketal of acetophenone, 14 ml butyl ether, and 6 ml glyme was saturated with nitrogen and then refluxed under nitrogen in the Strohmeier apparatus for 35 hours. The cooled reaction mixture was diluted with ether and filtered through a Celite bed with suction; the orange filtrate developed crystals when placed in the ice box. They were filtered and washed with hexane, 0.960 g, mp 103.3-105°; mp 103.5-105.5° (methylene chloride-hexane);

nmr ($CDCl_3$) δ 5.5 (m, 5), 4.4 (AB pattern, 2, J_{AB} = 2-4 Hz), 3.9 (q, 2, J = 7 Hz), and 1.3 ppm (m, 3).

(Acetophenone)tricarbonylchromium (33)

(α-Ethoxystyrene)tricarbonylchromium, 0.96 g, in 15 ml nitrogen-saturated absolute ethanol was treated with 18 ml nitrogen-saturated 0.5 N hydrochloric acid under nitrogen and let stand 14 hours. It was treated with excess water and the combined orange ethereal portions were dried ($MgSO_4$) and filtered. The solvent was removed on the rotary evaporator, and the residue crystallized; 0.430 g, mp 85.5-87.5° (hexane), lit. (13) mp 91.5-92°; nmr ($CDCl_3$) δ 5.2-6.2 (m, 5) and 2.5 ppm (s, 3).

(Methylbenzoate)tricarbonylchromium (49)

Prepared according to a modification of the procedure of Nicholls and Whiting (13).

A mixture of 8.358 g hexacarbonylchromium, 2 ml methyl benzoate, 8 ml glyme, and 8 ml hexane was refluxed under nitrogen in the Strohmeier apparatus for 37 hours. The cooled red-orange mixture was filtered through a Celite bed with suction and with several ether rinses. The solvent was removed on the rotary evaporator (aspirator vacuum) and the excess methyl benzoate was removed with a pump vacuum. The orange solid was washed with hexane on a sintered glass funnel to give 9.912 g.

(Benzoic acid)tricarbonylchromium (49)

Prepared according to the procedure of Nicholls and Whiting (13), mp 190° (dec), lit. (13), mp 194° (dec).

(Benzophenone)tricarbonylchromium (47)

Prepared according to a modification of the procedure of Holmes *et al*. (14).

A mixture of 2.186 g hexacarbonylchromium, 7.016 g benzophenone, 10 ml glyme, and 8 ml diglyme was refluxed under nitrogen in the Strohmeier apparatus for 10 hours. The cooled reaction mixture was filtered through a Celite bed with suction and with several ether rinses. The filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. Chromatography on silica gel gave an orange band which was eluted with 43% (v/v) benzene-pentane. The solvent was removed and the red solid was recrystallized from hexane, 0.304 g, mp 87-88°, lit. (14) mp 88-89°.

Benzoyl aziridine (39)

Prepared according to the procedure of Goldberg and Kelly (87), bp 80-82°/0.15 mm, lit. (87) mp 8-9°; nmr ($CDCl_3$) δ 7.95 (m, 2), 7.27 (m, 3), and 2.02 ppm (s, 4).

(Benzoylaziridine)tricarbonylchromium (**40**)

(Benzoic acid)tricarbonylchromium, 0.385 g, and 97 mg sodium methoxide were dissolved in 10 ml methanol (yellow), and then the excess solvent was removed on the rotary evaporator. To the residue was twice added 5 ml benzene with subsequent removal on the rotary evaporator (this procedure frees the reaction mixture from small amounts of methanol). The yellow residue was added to a solution of 1 ml oxalyl chloride and 10 µl pyridine in 5 ml benzene at 0°. The solvent was removed on the rotary evaporator and then 10 ml benzene was added to the orange-red residue, (benzoyl chloride)tricarbonylchromium. This slurry was slowly added to a stirring slurry of 1 g sodium bicarbonate and 2 ml aziridine in ice water (10 ml). To the orange reaction mixture was added excess water and ether. The ether layer was washed with water until the aqueous washings were colorless. The orange ethereal portion was dried ($MgSO_4$), filtered, and the solvent was removed from the filtrate to give an orange oil which crystallized on 4 hours standing in ice box. The solid was both rinsed onto a sintered glass funnel and washed with ice cold 1:10 benzene-hexane and sucked dry; 129 mg yellow orange powder, mp $98.2\text{-}100.2^\circ$; nmr ($CDCl_3$) δ 6.2 (d, 2, *J* = 6 Hz), 5.3 (m, 3), and 2.45 ppm (s, 4); mass spectrum *m/e* 283.

(Benzhydrol)tricarbonylchromium

Prepared according to the method of Holmes *et al.* (14), mp 99-101°, lit. (14) mp 99.5-100.5°.

(*p*-Methoxydiphenyl ketone)tricarbonylchromium

p-Methoxydiphenyl ketone, 4.956 g, 3.008 g hexacarbonylchromium, 10 ml diglyme, and 10 ml glyme refluxed under nitrogen in the Strohmeier apparatus for 21 hours. About 1/3 of the solvent was evaporated away from the system with a nitrogen stream and the reaction mixture was allowed to cool; it was filtered through a Celite bed with suction and with ether rinses. The ethereal filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. The red oil remaining was chromatographed on silica gel. The benzene eluant gave a 6:1 mixture of free to complexed material (by nmr of 5-6 and 7-8 ppm regions). The oil crystallized from methylene chloride-pentane on standing in ice box; mp 117-123° (methylene chloride-hexane); nmr ($CDCl_3$) δ 7.4 (AX pattern, 4, *J* = 9 Hz), 6.0 (m, 2), 5.4 (m, 3) and 3.8 ppm (s, 3); mp 122-124° (methylene chloride-hexane).

(*p*-Methoxydiphenylmethyl acetate)tricarbonylchromium

(*p*-Methoxydiphenyl ketone)tricarbonylchromium, 0.3251 g, stirring in 10 methanol, was treated with sodium borohydride portions until the orange color had become yellow. Excess water (200 ml) was added, and the suspension was filtered through paper; the yellow oil residue was taken up in ether, washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator to give a yellow oil which was treated, subsequently, with 10 ml of 1:1 acetic anhydride-pyridine. This solution was let stand at 0° for 16 hours. It was then poured onto 150 ml water and filtered through paper. The oily residue was washed exhaustively with water, then taken up in ether and methylene chloride, dried ($MgSO_4$), and filtered. The solvent was removed on the rotary evaporator; the residue crystallized on standing under hexane in the ice box; 0.206 g (56%), mp 99-101° (methylene chloride-hexane); nmr ($CDCl_3$) δ 7.1 (AA'BB' pattern, 4, $\underline{J}_{AB}$ = 8-9 Hz), 6.5 (s, 1), 5.3 (m, 5), 3.8 (s, 3), 1.85 (s, 3), and 1.3 ppm (0.5 impurity).

<u>Anal</u>. Calcd. for $C_{19}H_{16}CrO_5$: C, 60.64; H, 4.29. Found: C, 58.36; H, 4.33

<u>p</u>-Phenyl methyl benzoate

<u>p</u>-Biphenylcarboxylic acid, 26 g, was refluxed in 100 ml thionyl chloride until it dissolved; the excess thionyl chloride was then boiled off and the blackish residue was refluxed in methanol for 1/2 hour. The methanol was removed on the rotary evaporator and the residue was taken

up in methylene chloride and washed thoroughly with aqueous sodium bicarbonate, dried ($MgSO_4$), filtered, and the filtrate was evaporated to dryness on the rotary evaporator. The solid was recrystallized from benzene, 12.6 g, mp 114-119°, lit. (88) mp 116.5°.

p-((Phenyl)tricarbonylchromium) methyl benzoate

A mixture of 4.213 g hexacarbonylchromium, 4.363 g p-phenyl methyl benzoate, 5 ml dry diglyme, and 10 ml dry glyme was refluxed under nitrogen in the Strohmeier apparatus for 25 hours. The cooled reaction mixture was taken up in ether and filtered through a Celite bed with suction; the orange filtrate was thoroughly washed with water, dried ($MgSO_4$), filtered, and the filtrate was evaporated down to an orange solid with the rotary evaporator; then the solid was subjected to aspirator vacuum at 92° in order to assure that no hexacarbonyl remained (there was some). The solid was thoroughly swirled and shaken with 70 ml ether; the suspension was filtered to give a yellow solid, 2.376 g, mp 163-166.5°.

p-((Phenyl)tricarbonylchromium) benzyl alcohol

To a suspension of 0.118 g of lithium aluminum hydride stirring in 10 ml ether at -70° under a nitrogen atmosphere was added a suspension of 0.818 g p-((phenyl)tricarbonylchromium) methyl benzoate in 50 ml ether. The dry ice-acetone bath was removed and the temperature of the reaction contents was allowed to rise. At 15°, 5 ml ethanol was added slowly, and then the mixture was poured into cold dilute sulfuric acid and worked up by ether extraction. The extracts were washed with water, dilute sodium bicarbonate solution, water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator to give an oil which crystallized on the addition of ether-petroleum ether. The crystals were taken up in methylene chloride, the solution filtered, and the filtrate was boiled down to about 25 ml, 5 ml hexane was slowly added, and the solution was placed in the ice box. Subsequent seeding caused recrystallization, 172 mg, mp 95-96°; nmr ($CDCl_3$) δ 7.5 (AA'BB' pattern, 4, J_{AB} = 3-8 Hz), 5.3-5.8 (m, 5), 4.7 (s (broad), 2) and 1.9 ppm (s (very broad), 1.5).

p-((Phenyl)tricarbonylchromium) benzyl chloride (72)

p-((Phenyl)tricarbonylchromium) benzyl alcohol, 0.520 g, in 100 ml benzene, was shaken with 50 ml Lucas reagent ($ZnCl_2$-HCl) in a separatory funnel under nitrogen for a few minutes; the Lucas reagent was removed and replaced with 100 ml of fresh Lucas reagent and shaken again. After this Lucas reagent portion was removed, the yellow benzene solution was washed with water, sodium bicarbonate solution, water, dried ($MgSO_4$), filtered, and the filtrate was evaporated down to an orange oil in the rotary evaporator. On subjecting the oil to aspirator vacuum for a few minutes, it crystallized; 0.2445 g, mp 121-124° (ether-hexane); nmr ($CDCl_3$) δ 7.5 (AA'BB' pattern, 4, J_{AB} = 2-7 Hz), 5.2-5.8 (m, 5), 4.6 (s, 2), and 3.9 ppm (0.25, impurity).

Benzonorbornadiene (81)

Prepared by the procedure of Fieser and Haddadin (89), bp 93-96°/18-20 mm, lit. (90), bp 82.5-83.0°/12 mm; nmr (CCl_4) δ 6.8-7.1 (m, 4), 6.7 (m, 2), 5.8 (m, 2) and 2.2 ppm (m, 2).

Benzonorbornene (102)

Prepared by hydrogenation of benzonorbornadiene in ethanol over Pd/C, bp 104.5-106.5/26 mm, lit. (90), bp 78-79°/12 mm.

Benzonorbornen-2(*exo*)-yl acetate (86)

Prepared by the procedure of Bruson and Riener (91), bp 143-148°/14-15 mm, lit. (91), bp 84°/0.2 mm; nmr ($CDCl_3$) δ 7.0 (m, 4), 4.6 (m, 1), 3.25 (m, 2), 1.96 (s, 3), and 1.7-2.0 ppm (m, 4).

Benzonorbornen-2(*exo*)-ol (**95**)

Prepared by the lithium aluminum hydride reduction of benzonorbornen-2(*exo*)-yl acetate, mp 70.4-73°, lit. (92), mp 74.1-75.4°; nmr ($CDCl_3$) δ 7.0 (m, 4), 3.9 (m, 1), 3.2 (m, 2), 2.5 (s (broad), 1) and 1.6-2.2 ppm (m, 4); nmr ($CDCl_3$-D_2O) δ 7.0 (m, 4), 3.9 (m, 1), 3.2 (m, 2), and 1.6-2.2 ppm (m, 4).

Benzonorbornen-2(*exo*)-yl bromobenzenesulfonate (**98**)

Prepared by the procedure of Bartlett and Giddings (93), mp 80-81.5°, lit. (93) mp 82.2-84.4°.

Benzonorbornen-2(*endo*)-ol (**90**)

Prepared by the quinone procedure of Bartlett and Giddings (93), mp 74-75°, lit. (93), mp 74.5-75.4°; nmr ($CDCl_3$) δ 7.1 (m, 4), 4.8 (s, 1), 3.3 (m, 2), 2.0-2.5 (m, 1), 1.1-2.0 (m, 2) and 0.6-1.0 ppm (m, 2); nmr ($CDCl_3$-D_2O) δ 7.1 (m, 4), 4.8 (s, 1), 3.3 (m, 2), 2.0-2.5 (m, 1), 1.1-2.0 (m, 2), and 0.6-1.0 ppm (m, 1).

Benzonorbornen-2(*endo*)-yl bromobenzenesulfonate (**99**)

Prepared by the method of Bartlett and Giddings (93), mp 132-134.5°, lit. (93) mp 135.1-136.1°.

Anti-(benzonorbornen-2(exo)-yl acetate)tricarbonylchromium (87)

A mixture of 5 ml benzonorbornen-2(exo)-yl acetate and the (triacetonitrile)tricarbonylchromium from 2.277 g hexacarbonylchromium was refluxed for 3 hours in 15 ml dry dioxane under a nitrogen atmosphere and in the Strohmeier apparatus. The cooled reaction mixture was taken up in ether and washed thoroughly with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator to give a yellow oil. Upon chromatography on silica gel there was separated two yellow bands. The first band, quite faint, was eluted in 1:1 benzene-petroleum ether and was presumed to be (benzonorbornadiene)tricarbonylchromium. The second band was eluted in benzene and the solvent was removed on the rotary evaporator; crystallization from methylene chloride-hexane gave 1.390 g, mp 150-152°. The mother liquor was boiled down and yielded more solid, 0.184 g, mp 149.5-150.5° (methylene chloride-pet ether); nmr ($CDCl_3$) δ 5.3 (m, 4), 4.7 (m, 1), 3.1 (m, 2), 2.1 (s, 3), and 1.85 ppm (m, 4).

Anti-(benzonorbornen-2(exo)-ol)tricarbonylchromium (88)

To 1.28 g lithium aluminum hydride stirring in 30 ml tetrahydrofuran in an ice bath was slowly added, under a nitrogen atmosphere, a solution of 1.4363 g anti-(benzonorbornen-2(exo)-yl acetate)tricarbonylchromium in 25 ml tetrahydrofuran. After addition, the reaction mixture was allowed to continue stirring for 18 minutes while it warmed to room temperature. The excess hydride was destroyed with slow additions of water, and then with dilute hydrochloric acid. The reaction mixture was extracted with ether and the ether extracts were washed with water, dilute sodium bicarbonate solution, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator, 0.569 g, mp 130-132° (methylene chloride-pet ether); nmr ($CDCl_3$) δ 5.2 (m, 4), 4.0 (m, 1), 3.0 (m, 2), and 1.5-2.1 ppm (m, 5).

Anti-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium (89)

Anti-(benzonorbornen-(*exo*)-ol)tricarbonylchromium, 0.4633 g, and 0.7825 g bromobenzenesulfonyl chloride were added to 20 ml dry, cold, and nitrogen-saturated pyridine. The reaction mixture was then stoppered and let stand at about 0° for 24 hours. The green solution was poured onto excess cold water, filtered, and the residue was thoroughly washed with water. The residue was taken up in ether, washed with sodium bicarbonate solution, dried ($MgSO_4$), filtered, and the solvent removed on the rotary evaporator to give an amorphous material composed of white and yellow solid. The mixture was washed, on the filter, with an ether-pentane solvent mixture until all the white material had been dissolved away, leaving 0.2057 g (26%) of yellow material, mp ~148°; nmr ($CDCl_3$) δ 7.7 (s, 4), 5.2 (m, 4), 4.9 (m, 1), 3.15 (m, 2), and 1.5-2.1 ppm (m, 5); mass spectrum *m/e* 514, 516.

Syn-(benzonorbornadiene)tricarbonylchromium (83)

A mixture of 5 ml benzonorbornadiene and the (triacetonitrile)tricarbonylchromium from 2.973 g hexacarbonylchromium were refluxed in 10 ml dry dioxane, under nitrogen, in the Strohmeier apparatus, for 9 minutes. The brownish-orange solution was allowed to cool to room temperature. It was then taken up in ether and filtered, with suction, through a Celite bed; the orange-yellow filtrate was washed with 3 X 150 ml water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator, whereupon crystals formed. The crystals were collected on a sintered glass funnel and washed thoroughly with hexane, 1.271 g, mp 132°. The hexane wash was evaporated to a small volume to yield 0.2451 g, mp 132°; nmr ($CDCl_3$) δ 6.85 (m, 2), 5.8 (m, 2), 5.1 (m, 2), 3.7 (m, 2), and 2.3 ppm (m, 2).

Syn-(benzonorbornen-2(*exo*)-ol)tricarbonylchromium (84)

To 1.392 *syn*-(benzonorbornadiene)tricarbonylchromium, under nitrogen, was added, while stirring, 54.2 mg sodium borohydride and then 231 μl boron trifluoride etherate; the mixture was allowed to stir for 65 minutes. The clear yellow solution was treated with 0.50 ml water while being cooled in an ice bath, 0.53 ml 3 N sodium hydroxide, and then 0.60 ml 30% hydrogen peroxide. A yellow green precipitate formed. Stirring was continued 45 minutes (1.5 ml diglyme was added initially to facilitate stirring). The reaction mixture, with the aid of ether rinses, was poured onto 200 ml nitrogen-saturated water. The aqueous portion was extracted with ether until the ether extracts were colorless (3 x 100 ml). The combined yellow ether extracts were washed with 2 x 100 ml nitrogen-saturated water, 100 ml sodium bicarbonate solution, 100 ml water, dried ($MgSO_4$), and then filtered. The filtrate was subjected to rotary evaporation to give a yellow solid which was then washed thoroughly with pentane until the washings were colorless. The solid mass was collected upon a sintered glass funnel, and washed with pentane, 1.0389 g (70%), mp 148° (dec); nmr ($CDCl_3$) δ 5.5 (m, 2), 5.1 (m, 2), 4.3 (m, 1), 3.0 (m, 2), and 1.0-2.5 ppm (m, 5).

Syn-(benzonorbornen-2(exo)-yl bromobenzenesulfonate)tricarbonylchromium (85)

To a stirred solution of 0.3067 g syn-(benzonorbornen-2(exo)-ol)tricarbonylchromium in 5 ml dry tetrahydrofuran was added, under nitrogen, 0.715 ml of 1.6 M n-butyl lithium; after the addition, stirring was continued for

12 minutes. The reaction mixture was then slowly treated with a solution of 0.298 g bromobenzenesulfonyl chloride in 7 ml dry tetrahydrofuran. The yellow solution was warmed in a 50° water bath briefly, refluxed for 5 minutes, and then let cool. The reaction mixture, using ether rinses, was then poured into a rapidly stirring ice-water (100 ml) mixture; ether was added and the mixture was shaken. The water layer was removed and extracted with ether (3 x 80 ml); the combined ether layers were washed with 100 ml nitrogen-saturated water, 100 ml sodium bicarbonate solution, dried ($MgSO_4$), and filtered. The solvent was removed on the rotary evaporator. The yellow oil smelled like bromobenzenesulfonyl chloride so it was swirled in 3 x 100 ml pentane, treated with a little 1:1 ether-pentane and allowed to stand in ice box overnight. The yellow, finely crystalline material was collected and washed with pentane, 0.2268 g (43%), mp 127° (dec); nmr ($CDCl_3$) δ 7.8 (m, 4), 5.5 (m, 2), 5.1 (m, 2), 4.8 (m, 1), 3.3 (m, 1), and 2.1 ppm (m, 4); mass spectrum *m/e* 514, 516.

Anti-(benzonorbornadiene)tricarbonylchromium (93) and *syn*-(benzonorbornen-(*exo*)-yl acetate)tricarbonylchromium (96)

A mixture of 0.9698 g *syn*-(benzonorbornadiene)tricarbonylchromium, 15 ml glacial acetic acid, 0.4 ml water, 0.4 ml conc. sulfuric acid, and 3 ml dioxane was saturated with nitrogen, and placed in a 60-70° bath for 10 hours.

The reaction mixture was very green with green solid in suspension; it was poured into a separatory funnel using water and ether rinses and shaken; the water layer was removed and extracted with 20 ml ether. The combined ethereal portions were thoroughly washed with nitrogen-saturated water, sodium bicarbonate solution, water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. Chromatography of the residue on silica gel gave two yellow bands.

The first band (1:1 benzene-hexane) yielded a yellow oil which crystallized from hexane as a yellow powder, 0.103 g, mp 127.5-129.5°; nmr ($CDCl_3$) δ 6.6 (m, 2), 5.3 (m, 4), 3.7 (m, 2), 2.5 (m, 1), and 2.25 ppm (m, 1).

The assignment on the basis of solvent effects on the nmr spectrum was _anti_-(benzonorbornadiene)tricarbonylchromium.

The second band (chloroform-methanol) yielded a yellow oil which crystallized from ether-hexane on standing in the ice box; the crystals were recrystallized from methylene chloride-hexane, 44 mg, mp 143-144°; nmr ($CDCl_3$) δ 5.6 (m, 2), 5.1 (m, 3), 3.1 (m, 2), and 1.7-2.4 ppm (m, 7). The assignment on the basis of solvent effects on the nmr spectrum is _syn_-(benzonorbornen-(_exo_)-yl acetate)-tricarbonylchromium.

Anti-(benzonorbornen-2(endo)-ol)tricarbonylchromium (91)

A mixture of (triacetonitrile)tricarbonylchromium from 2.06 g hexacarbonylchromium and 3.30 g benzonorbornen-2-(endo)-ol was refluxed in 15 ml dry dioxane, under nitrogen, in the Strohmeier apparatus, for 1/2 hour. The clear dark red solution was allowed to cool to room temperature and was filtered with suction through a Celite bed. The filtrate was washed with water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. On standing under a small amount of 10% ether-pet ether in the ice box, the oil crystallized; mp 110-132° (methylene chloride-pet ether). The crude solid was washed thoroughly with pet ether, mp 99.9-101°. It was then stirred vigorously overnight with 100 ml pentane, mp 118-125°. Recrystallization from ether-pentane gave mp 135-137°, 0.7678 g (28%). The mother liquor yielded 0.1774 g, mp 133.5-135° for a total yield of 0.9452 g, or 34%, of what was presumably anti-(benzonorbornen-2(endo)-ol)tricarbonylchromium.

Anti-(benzonorbornen-2(endo)-yl bromobenzenesulfonate)tricarbonylchromium (92)

To a stirred solution of 0.7640 g anti-(benzonorbornen-2(endo)-ol)tricarbonylchromium in 5 ml dry tetrahydrofuran under a nitrogen atmosphere was slowly added, at room temperature, 1.78 ml 1.6 M n-butyl lithium. The reaction mixture was allowed to continue stirring a few minutes and then a solution of 0.743 g bromobenzenesulfonyl chloride in 15 ml dry tetrahydrofuran was slowly added. After the addition, stirring was continued 20 minutes, the greenish yellow solution was poured onto 300 ml ice-cold water, ether added, and the mixture was shaken; the water layer was removed and the ether layer was washed with 200 ml ice-cold water, and dried ($MgSO_4$), filtered, and the solvent was evaporated off the filtrate on the rotary evaporator, whereupon crystals formed. These crystals were taken up in ether, in which they were sparingly soluble, and collected on a sintered glass funnel, 0.3262 g (25%), mp 170° (dec); nmr ($CDCl_3$) δ 7.7 (s, 4), 5.0-5.7 (m, 5), 3.3-3.6 (m, 1), 3.0-3.2 (m, 1), and 1.0-2.7 ppm (m, 4); mass spectrum *m/e* 514, 516.

Benzyl methyl ether

Prepared by refluxing benzyl chloride in sodium methoxide-methanol overnight, bp 64-65°/17 mm, lit. (94) bp 170-171°.

(Diglyme)tricarbonylmolybdenum

Prepared by the procedure of Werner and Coffield (95).

(Benzyl methyl ether)tricarbonylmolybdenum

Under nitrogen, 2.1615 g (diglyme)tricarbonylmolybdenum, 15 ml nitrogen-saturated hexane, and 2 ml nitrogen-saturated benzyl methyl ether were placed in a 50 ml round bottom flask equipped with side arm. The flask was attached to the Strohmeier apparatus, under nitrogen, and then refluxed for 30 minutes; under nitrogen, in a glove bag, the hot reaction mixture was filtered through a Celite bed with suction and with nitrogen-saturated pentane rinses. The crystalline filtrate was transferred to a round bottom flask with nitrogen-saturated pentane rinses, the flask was securely stoppered, and let stand in ice box for a few hours. The crystals were collected under nitrogen, in a glove bag, by filtration of the mixture through a sintered glass funnel followed by nitrogen-saturated pentane washes, 1.15 g (55%), mp 65° (dec). Under nitrogen, in a glove bag, the material was dissolved in the minimum amount of nitrogen-saturated methylene chloride, twice that amount of nitrogen-saturated pentane was added, and the solution was filtered through cotton, adding pentane slowly until the filtrate was cloudy. The filtrate was securely stoppered and placed in ice box overnight. Under nitrogen, in a glove bag, the clear yellow supernatant liquid was poured off, and the yellow crystals were rinsed onto a sintered glass funnel with nitrogen-saturated pentane.

The solid mass was sucked dry, under nitrogen, and dried in vacuo for 1/2 hour to give 0.685 g, of air sensitive yellow crystals, mp 69-72° (dec), nmr (nitrogen-saturated $CDCl_3$ in a nitrogen-filled nmr tube) δ5.6 (m, 5), 4.1 (s, 2), and 3.4 ppm (s, 3).

(Benzyl methyl ether)tricarbonyltungsten

A mixture of 1.18 g hexacarbonyltungsten and 15 ml acetonitrile was refluxed in the Strohmeier apparatus, under nitrogen, for 30 hours. The excess acetonitrile was blown off with a nitrogen stream and to the (triacetonitrile)tricarbonyltungsten (71) was added 2 ml benzyl methyl ether, 5 ml hexane, and 10 ml cyclohexane. This mixture was refluxed, under nitrogen, for 45 minutes. The blackish warm reaction mixture, under nitrogen in a glove bag, was filtered through a Celite bed with suction and with hexane rinses. The filtrate, crystalline, was transferred to a 50 ml round bottom flask, stoppered, and placed in the ice box. The crystals were filtered out, under nitrogen, with hexane rinses to give air-stable material, 0.63 g (48%), mp 83-85°; nmr ($CDCl_3$) δ 5.4 (m, 5), 4.2 (s, 2), and 3.45 ppm (s, 3). Recrystallization from methylene chloride-pentane, and subsequent washing with cold 95% ethanol, and drying in vacuo, gave mp 84.5-86.5°.

Thermodynamic-Control-Complexation of Benzonorbornadiene and Benzonorbornene

Syn- and *anti*-(benzonorbornadiene)tricarbonylchromium

A mixture of 5 ml benzonorbornadiene and the (triacetonitrile)tricarbonylchromium from 2.1951 g hexacarbonylchromium in 15 ml dioxane was refluxed 195 minutes, under nitrogen, in the Strohmeier apparatus; the cooled reaction mixture was filtered through a Celite bed with suction and with ether rinses; the filtrate was subjected to rotary evaporation; the residue was crystallized from methylene-pet ether, mp 105-115°; nmr ($CDCl_3$) indicated that the ratio of *anti*- to *syn*-complex was 71/33.

Syn- and *anti*-(benzonorbornene)tricarbonylchromium

A mixture of 5 ml benzonorbornene and the (triacetonitrile)tricarbonylchromium from 2.798 g hexacarbonylchromium in 12 ml dioxane was refluxed 50 minutes, under nitrogen, in the Strohmeier apparatus; the cooled reaction mixture was filtered through a Celite bed with suction and with ether rinses; the filtrate was subjected to rotary evaporation; the residue was about 6:1 *anti*- to *syn*-complex with much free benzonorbornene present; the residue was washed in cold pentane; residue was 6:1 *anti*- to *syn*-complex by nmr.

Determination of $p\underline{K}_{R^+}$ for (Benzyl)tricarbonylchromium Cations

Preparation of sulfuric acid-water solutions

Sulfuric acid, 96.8% assay H_2SO_4, was poured onto a known weight of ice until the desired concentration, by weight percent, was attained.

Spectral technique

Into the reference and sample compartments of a Cary 14 spectrophotometer were placed 5 cm-long, 15.5 ml, cells; in the reference cell was water; into the sample cell was placed sulfuric acid of known concentration. The base line was adjusted to 0.05 absorbance units at the wavelength to be examined. (Benzyl alcohol)tricarbonylchromium, 51.9 mg, was dissolved in 0.50 ml 95% ethanol in a microculture tube which was then sealed with a sealed stopper. With a 10 μl syringe, 10.0 μl of the solution was withdrawn and slowly injected into the cell containing the thoroughly nitrogen-flushed sulfuric acid and a vigorously spinning stir bar. At the half-way joint of the injection, a timer was started. The solution was quickly placed in the sample chamber of the spectrophotometer, and the chart drive was initiated, while remaining at 513.5 mμ, the λ_{max} for the cation in the visible region (in this way, the decay of the absorption of the cation was automatically recorded). The time was recorded on the chart and an extrapolation of the decay curve to time zero, the time of mixing, gave the absorption of the cation. The values obtained, Table 37, were used in making the plots of ϵ vs. C_o (Figure 1).

Table 37. The time-zero absorption at 513.5 mμ for the (benzyl)tricarbonylchromium cation in aqueous sulfuric acid

% H_2SO_4	C_o	$A_{t=0}$
0	--	0.026
44.0	- 5.48	0.015
65.0	-10.22	0.020
67.0	-10.74	0.056
69.1	-11.26	0.094
71.1	-11.78	0.220
73.0	-12.30	0.358
75.0	-12.82	0.453
80.0	-14.12	0.454
87.0	-15.86	0.455
96.8	-18.84	0.425

Recovery experiments

Reversibility of ultraviolet spectrum   Forty microliters of a solution of 31.7 mg (benzyl alcohol)tricarbonylchromium in 5.0 ml 95% ethanol solution was injected slowly into 10.0 ml stirring 82.6% sulfuric acid (violet), and then immediately poured onto 10.0 g ice to give a 52.5% sulfuric acid solution (yellow). The ultraviolet region (no absorption in the visible) was examined and showed that the alcohol was the absorbing specie.

Recovery of (p-methylbenzyl alcohol)tricarbonylchromium from its solution in 51.0% sulfuric acid   A solution of 0.1655 g (p-methylbenzyl alcohol)tricarbonylchromium in 2 ml 95% ethanol was slowly injected into 100 ml of 51.0% sulfuric acid stirring at 5°; this yellow solution was quickly poured into 200 g ice water, and extracted with ether. The combined ether portions were washed with water and dilute sodium bicarbonate solution, dried ($MgSO_4$), filtered, and the solvent removed on the rotary evaporator. The solid residue was recrystallized from methylene chloride-pentane to give 0.1039 g (63%) of yellow material which was identified as the starting material by its melting point, 77-80°, and its mixed melting point, 79.5-83°, with authentic alcohol, and its nmr.

Recovery of (benzyl alcohol)tricarbonylchromium from its solution in 85% sulfuric acid   A solution of 0.2200 g (benzyl alcohol)tricarbonylchromium in 12 ml 95% ethanol was slowly injected into 400 ml of cold (5°) and vigorously stirred 85% sulfuric acid through which was continually bubbled a rapidly flowing nitrogen stream. The characteristic violet color was intense and seemingly stable for at least several seconds. This solution was immediately poured into about 600 g ice. The yellow solution was extracted with ether (3 x 200 ml) and the combined ether portions were washed with 200 ml dilute sodium bicarbonate solution, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. Pump vacuum was applied to the yellow solid to remove all traces of ether; the addition of 16 µl cyclohexane to the deuterochloroform solution resulted in the areas of cyclohexane to benzylic methylene nmr absorptions of 68 to 53, corresponding to a 76.7% recovery of (benzyl alcohol)tricarbonylchromium. Isolation of the alcohol from methylene chloride-hexane gave 122.3 mg, mp 91-93° (mixed mp 92.1-94.5° with authentic alcohol), whose nmr in deuterochloroform was indistinguishable from that of the authentic alcohol. The mother liquor gave 5.5 mg, mp 86-90°, for a total of 127.8 mg or 58.2% recovery.

Isolation and identification of cation decomposite

A solution of 0.2044 g (p-methylbenzyl alcohol)tricarbonylchromium in 1.5 ml 95% ethanol was very rapidly injected, under nitrogen, into 40 ml of nitrogen-saturated 94% sulfuric acid which was rapidly stirred at room temperature. The violet color gave way to a reddish brown within 10 seconds. The reaction mixture was poured out upon about 200 g ice and this solution was extracted with ether portions which were combined and washed with nitrogen saturated water, dilute sodium bicarbonate, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator to give a yellow solid, 0.1161 g, mp 179-230° (dec); 52.8 mg, mp 185° (dec) (acetone-hexane). This material is insoluble in ethanol, acetic acid, chloroform, ether, and hot 94% sulfuric acid (up to 70°). The mass spectrum showed m/e 482; nmr (pyridine) δ 5.45 (m, 4), 2.6 (s, 2), and 2.0 ppm (s, 3), consistent with bis((p-methylbenzyl)tricarbonylchromium).

Determination of pK_{BH^+} of (α-Hydroxybenzyl)tricarbonylchromium Cations

Spectral technique

Into 10.0 ml of stirring, nitrogen-saturated, sulfuric acid of known concentration was injected 5-20 µl of 0.10-0.20 M ethanolic solutions of the benzoyl compounds; a timer was initiated at the half-way point of the injection. The solution was quickly poured into a 1 cm cell and this cell was quickly placed in the Cary 14 spectrophotometer and the chart drive was initiated, while remaining at a convenient wavelength. In this way, the decay of the absorption of the cation was automatically recorded. The time after mixing was recorded on the chart and an extrapolation of the decay curve to time zero, the time of mixing, gave the sum of the absorptions of the cation and its conjugate base (benzaldehyde in this case). The values obtained, Table 38, were used in making the plot of $A_{296} - A_{321}$ and $A_{478} - A_{321}$ vs. H_o. The absorptions at 296 mμ and 478 mμ are characteristic of the cation (increase with increasing acid), while that at 321 mμ is characteristic of the conjugate base (increase with decreasing acid).

Recovery experiments

(Benzoic acid)tricarbonylchromium (Benzoic acid)tricarbonylchromium, 0.2026 g, in 8 ml 95% ethanol, was slowly injected into 100 ml of cold, vigorously stirring, 96.8% sulfuric acid through which was bubbled a nitrogen stream. The dark red-brown solution was immediately poured upon about 300 g ice (orange); the aqueous mixture was extracted with ether (3 x 100 ml). The combined yellow ether extracts were washed with 100 ml water, and then

Table 38. The time-zero absorptions for the (benzaldehyde-α-hydroxybenzyl cation)tricarbonylchromium system in various sulfuric acid-water mixtures[a]

% H_2SO_4	H_o	A_{296}	A_{321}	A_{478}	$A_{296}-A_{321}$	$A_{478}-A_{321}$
0.0	-0.83	0.715	1.270	0.121	-0.555	-1.149
35.0	-1.91	0.708	1.289	0.162	-0.581	-1.127
51.0	-3.34	0.593	0.970	0.200	-0.377	-0.770
61.1	-4.45	0.620	1.346	0.372	-0.726	-0.974
65.0	-4.93	0.595	0.939	0.260	-0.344	-0.679
67.0	-5.17	0.748	1.064	0.354	-0.316	-0.711
69.1	-5.42	0.70	0.90	0.351	-0.20	-0.55
71.1	-5.67	0.775	0.880	0.416	-0.105	-0.464
73.0	-5.91	0.871	0.852	0.423	0.019	-0.429
75.0	-6.16	1.125	0.952	0.533	0.26	-0.63
77.5	-6.49	1.150	0.866	0.641	0.284	-0.225
80.0	-6.82	1.223	0.858	0.58	0.365	-0.278
82.6	-7.24	1.41	0.8	0.45	0.6	-0.35
85.0	-7.62	1.425	0.734	0.61	0.691	-0.124
87.0	-7.84	1.41	0.740	0.625	0.67	-0.115
87.0	-7.84	1.401	0.833	0.578	0.568	-0.255
92.0	-8.40	1.6	0.8	0.6	0.8	-0.2

[a] All wavelengths given in microns.

100 ml saturated sodium chloride solution, dried ($MgSO_4$), filtered; the solvent was removed on the rotary evaporator. The red solid was recrystallized to give 0.1070 g (53%) of red material, mp 189° (dec). The mixed mp with (benzoic acid)tricarbonylchromium was 188.5° (dec). The infrared spectrum of this material was superimposable with that of the starting material.

(p-Methyl N,N-dimethylbenzamide)tricarbonylchromium (p-Methyl N,N-dimethylbenzamide)tricarbonylchromium, 0.2338 g, in about 8 ml of 95% ethanol, was slowly injected into 100 ml of cold, vigorously stirring, 97.1% sulfuric acid through which was bubbled a nitrogen stream. The deep orange colored solution was quickly poured upon 300 g of ice; the aqueous mixture was extracted with ether (4 x 100 ml); the combined ether portions were washed with dilute sodium bicarbonate solution, dried ($MgSO_4$), and filtered; the solvent was removed on the rotary evaporator. The solid was recrystallized from methylene chloride-hexane to give 0.1344 g (58%) of yellow material, mp 141.5° (dec). Mixed mp with (p-methyl N,N-dimethylbenzamide) was 141.8° (dec). The infrared spectrum of this material was superimposable with that of the starting material.

(Acetophenone)tricarbonylchromium (Acetophenone)tricarbonylchromium, 0.2703 g, in about 3 ml 95% ethanol, was slowly injected into 100 ml of cold, vigorously stirring, 97.1% sulfuric acid through which was bubbled a nitrogen stream. The blood red solution was quickly poured upon about 200 g of ice; the aqueous mixture was extracted with ether (3 x 100 ml); the combined ether portions were washed with dilute sodium bicarbonate solution, dried ($MgSO_4$), filtered; the solvent was removed on the rotary evaporator. The red oil was crystallized from methylene chloride-hexane to give 0.1950 g (72%) red material, mp 83.5-86°. Mixed mp with (acetophenone)tricarbonylchromium was 84.5-86.5°. The infrared spectrum of this material was superimposable with that of the starting material.

(Benzaldehyde)tricarbonylchromium (Benzaldehyde)tricarbonylchromium, 0.1856 g, in 9 ml 95% ethanol, was slowly injected into 100 ml of cold, vigorously stirring, 97.1% sulfuric acid through which was bubbled a nitrogen stream. The dark yellow-brown solution was quickly poured upon about 200 g ice; the aqueous mixture was extracted with ether (3 x 100 ml); the combined ether portions were washed with dilute sodium bicarbonate, dried ($MgSO_4$), and filtered; the solvent was removed on the rotary evaporator to give a red oil which was crystallized from methylene chloride-hexane to give 0.1237 g (68%) of red material, mp 74-77°.

The mixed mp with (benzaldehyde)tricarbonylchromium was 78-83°. The infrared spectrum of this material was superimposable with that of starting material.

<u>(Benzophenone)tricarbonylchromium</u> (Benzophenone)tricarbonylchromium, 0.2038 g, in 8 ml 95% ethanol, was slowly injected into 100 ml of cold, vigorously stirring, 97.1% sulfuric acid through which was bubbled a nitrogen stream. The deep purple solution was quickly poured upon about 200 g ice; the aqueous mixture was extracted with ether (2 x 100 ml); the combined ether portions were washed with dilute sodium bicarbonate, dried ($MgSO_4$), and filtered; the solvent was removed on the rotary evaporator to give a red oil which was crystallized from methylene chloride-hexane to give 0.1560 g (77%) of red material, mp 86.5-88.7°. The mixed mp with (benzophenone)tricarbonylchromium was 85.8-88.5°. The infrared spectrum of this material was superimposable with that of starting material.

Determination of $p\underline{K}_{R^+}$ for (Diphenylmethyl)tricarbonylchromium Cations

<u>Spectral technique</u>

Into a 15.5 ml, 5 cm, ultraviolet-visible cell containing a stirred, nitrogen-saturated, sulfuric acid-water mixture of known proportions was injected 8-20 µl of a 7.54 <u>M</u> solution of the complex in ethanol; a timer was initiated at the half-way point of the injection. The cell was quickly placed in the spectrophotometer, and the chart drive was initiated, while remaining at 442 mμ, the λ_{max} for the unsubstituted cation in the visible.

At high acid concentrations (80-100%) the absorption increased rapidly with time, eventually attaining the value characteristic of the free cation. At moderate acid concentrations (60-80%) the absorption decreased with time; if, however, nitrogen-saturation was not complete, these absorptions would also rise, but very slowly.

The transformation of (diphenylmethyl)tricarbonylchromium cation to diphenylmethyl cation was characterized, visually, by a change in color from an orange-yellow to a yellow. The (*p*-methoxydiphenylmethyl)tricarbonylchromium cation, when first formed, was a deep blue-purple, which gradually became grey, then green, and finally, a bright yellow, the color of the free cation. Because the (*p*-methoxydiphenylmethyl)tricarbonylchromium cation was formed in much weaker acid than the unsubstituted complexed cation, decomposition to the free cation was much less of a problem than with the (diphenylmethyl)tricarbonylchromium cation.

Recovery experiment

A solution of 0.208 g (diphenylmethanol)tricarbonylchromium in 3 ml glacial acetic acid was slowly injected into rapidly stirring, cold, 69% sulfuric acid (in which the complexed cation is almost 100% formed; see Figure 16), through which was bubbled a nitrogen stream. The brown-orange, rapidly fading, solution was poured quickly onto 500 g ice (yellow) and the organic material was extracted out with ether. The ether portion was washed with water, dilute sodium bicarbonate solution, water, dried ($MgSO_4$), filtered, and the solvent was removed on the rotary evaporator. The yellow oil was crystallized from methylene chloride-hexane, 0.0928 g, mp 97.5-100°; mixed mp with authentic (diphenylmethanol)tricarbonylchromium was 98-101°; ir (KBr) 1960 (40% transmission), 1890, 1700 (60%), 1600, 1350 cm^{-1}; comparison with ir of (diphenylmethanol)tricarbonylchromium, 1960 (70% transmission), 1890 (70%), 1700 (40%), 1600, 1350, led to the conclusion that the material recovered is 40% (diphenylmethanol)tricarbonylchromium, 60% diphenylmethanol; the recovery was then 18% complete.

Solvolyses

Solvolyses of the sulfonates were carried out in 70% acetone-water (v/v).

Benzonorbornen-2(endo)-yl bromobenzenesulfonate, 98, *anti*-(benzonorbornen-2(*exo*)-yl bromobenzenesulfonate)tricarbonylchromium, **89**, and *anti*-(benzonorbornen-2(*endo*)-yl bromobenzenesulfonate)tricarbonylchromium, **92**, were solvolyzed in sealed tubes. Into each of nine or ten, 30-cm-long, hard glass tubes, 9 mm OD X 6 mm ID, which were sealed at one end, were placed 0.9-1.0 ml of a 70% aqueous acetone solution, 5 m*M* in sulfonate. Each tube was attached to the vacuum line, immersed in liquid nitrogen until the contents were thoroughly frozen and then evacuated. The access to the vacuum pump was closed with a stopcock, the contents were thawed, sometimes by gentle heating with a flame, and the freeze-evacuate-thaw procedure was repeated. Finally, the tube was again immersed in liquid nitrogen, access to the vacuum pump was established, and the tube was sealed so as to give a 20 cm length. The tubes were placed in a mineral oil bath maintained at a desired temperature; a timer was initiated. Tubes were removed, the time noted, and the tubes were immediately cooled with an acetone wash (removed mineral oil), and then immersion under a cold water tap. The tube was broken; 0.55-0.6 ml was removed with a 1 ml syringe, and 0.50 ml was delivered into 5 or 10 ml acetone in which was 8-10 drops of bromothymol blue and a small stirring bar. Into the solution was vigorously bubbled a fine nitrogen stream, the stir bar was spun, and the contents were very rapidly titrated to the first blue-green with 0.00122-0.00124 N calcium hydroxide (standardization against 0.00481 N aqueous sulfamic acid was repeated at 1-3 day intervals) which was stored in a 2000 ml bottle equipped with ascarite to minimize contamination by atmospheric carbon dioxide. The blue-green rapidly faded to an eventual yellow due to absorption of atmospheric (and human) carbon dioxide.

Benzonorbornen-2(exo)-yl bromobenzenesulfonate and syn-(benzonorbornen-2(exo)-yl bromobenzenesulfonate)tricarbonylchromium were solvolyzed in convenient unsealed containers because the rapid solvolysis rate of these two esters permitted the presence of oxygen. Into a 10 ml volumetric flask was placed about 9.5 ml 70% aqueous acetone, and then a round rubber disc (cut from a sealed stopper) was jabbed into the neck so that it made a tight seal just above the 10.0 ml mark; a syringe needle protruding through the disc relieved air pressure as it was being thrust downward. The flask was placed in the bath at the desired temperature, the contents were allowed to equilibrate, an air or nitrogen stream was directed onto the rubber disc in order to dry the top part thoroughly, and then about 0.05 mmole of sulfonate was placed on top of the dried disc. The flask was then sealed snugly with a sealed stopper through which protruded a syringe needle that relieved the air pressure as the seal was being made. At this point, a 1 ml syringe, the plunger being held down tightly, was jabbed through the top sealed stopper, and then the disc was shoved down, permitting the sulfonate to mix with the solvent. With the syringe needle still inside the flask, the contents were shaken until dissolution was attained. The first 0.55-0.6 ml aliquot was taken out and treated as above. This method is a good one for runs which occur at temperatures no higher than would create solvent vapor pressures of about two atmospheres (the sealed stopper was blown out at about 100°).

Most infinity titers were within 10% of the calculated value; in a very slow run, where oxidation of the complex was important, the theoretical infinity was used in the calculations (Table 39).

The plot of log $(V_\infty - V_t)$, where V_t was the volume of base needed to titrate the acid produced in time, t, of reaction time, vs. t gave straight lines through at least one half-life in every case. The time at which the term $(V_\infty - V_t)$ had become 1/2 its value at time = 0 was equal to the half-life, $t_{1/2}$, of the reaction. The rate constant is then given by $0.693/t_{1/2}$.

p-((Phenyl)tricarbonylchromium)benzyl chloride, 72, and benzyl chloride were solvolyzed in 80% aqueous acetone (v/v), at 76.59°, in a stoppered volumetric flask (solvent

Table 39. Experimental parameters for solvolyses in 70% aqueous acetone

Sulfonate	Conc.[a]	Temp.[b]	Calc V_∞[c]	Obs V_∞[d]	Deviation[e]	Remarks
exo (**98**)	5.82	40.89	3.65	4.05	10.9	
exo (**98**)	5.28	60.01	3.33	3.35	0.6	
exo (**98**)	3.74	80.00	2.42	2.50	3.3	
endo (**99**)	6.56	100.00	4.21	3.87	8.1	
endo (**99**)	9.23	120.2	5.70	4.55	20.2	
anti-*exo* (**89**)	4.92	80.00	4.27	5.71	33.7	
anti-*exo* (**89**)	5.78	100.00	4.99	5.34	7.0	Decomposition first observed at 6 half-lives

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[a] In mmoles/l.

[b] In degrees centrigrade.

[c] The calculated infinity titer expressed in ml of base (0.00122-0.00124 *N*); includes the blank for the 5 or 10 ml acetone used in quenching the solvolyses (the blank usually consumed about 0.3 ml base); for a 1.0 ml aliquot.

[d] The experimental infinity (> 10 half-lives) titer expressed in ml of base; for a 1.0 ml aliquot.

[e] Calculated as follows: deviation = ((obs V_∞ - calc V_∞)/calc V_∞) x 100.

Table 39 (Cont.)

Sulfonate	Conc.[a]	Temp.[b]	Calc V_∞[c]	Obs V_∞[d]	Deviation[e]	Remarks
syn-*exo* (**85**)	4.69	60.00	3.95	3.95	0.0	
syn-*exo* (**85**)	5.52	80.00	3.52	3.27	9.3	
anti-*endo* (**92**)	5.43	80.00	5.10	--[f]	--	Decomposition first observed at 0.4 half-lives
anti-*endo* (**92**)	4.25	100.00	4.98	4.76[g]	4.4	Decomposition first observed at 0.7 half-lives

[f] The calculated infinity titer was used to derive the rate constant.

[g] A 0.80 ml aliquot of 3 hour old solvolysis solution was delivered into 0.4 ml water in another tube, degassed, sealed, and replaced in the bath. The nearly colorless (decomposed) solution was removed at 20 hours, which was estimated to be 10 half-lives for 47% aqueous acetone, and analyzed for acid as above.

not-degassed). The procedure for determining acid content was as above. At 76.59°, the rate constant for the complex was 2.7 x 10^{-6} sec^{-1} (one determination). Oxidation of the complex was observed, and since such oxidation would lead to the more rapidly solvolyzing p-phenylbenzyl chloride, the results are tenuous.

Products of solvolyses

Into a 20 mm OD hard glass tube sealed at one end was placed 88.9 mg syn-(benzonorbornen-2(exo)-yl bromobenzenesulfonate)tricarbonylchromium and 30 ml 70% aqueous acetone. The tube was connected to a vacuum line, the contents were frozen in liquid nitrogen, the tube was evacuated, and then the contents were allowed to thaw; the freeze-evacuate-thaw procedure was repeated, and the contents were again frozen and the tube was sealed at 30 cm length. The tube was placed in running hot water at 55° for 65 minutes (ten half-lives), removed, and let cool. The tube was broken by touching a red hot wire (5 volts on Variac) to the glass followed by dabs of water. The contents were poured onto 300 ml of nitrogen saturated water, 50 ml methylene chloride was added, and the mixture was shaken. The methylene chloride layer was drawn off and combined with a methylene chloride extract of the aqueous layer. The methylene chloride portion was washed with 200 ml nitrogen-saturated water, 200 ml nitrogen-saturated potassium bicarbonate solution, dried ($MgSO_4$), filtered, and the solvent was removed in the rotary evaporator to give a yellow solid; nmr ($CDCl_3$) was superimposable with the nmr of _syn_-(benzonorbornen-2(_exo_)-ol)tricarbonylchromium except for small peaks at δ 6.6, 7.1, and 7.75 ppm, which may have represented 2.7% of the starting material, 5.7% of benzonorbornen-2(_exo_)-ol. The remainder, 91.5%, is the _syn_-_exo_ alcohol.

Similarly, there was solvolyzed 71.5 mg _anti_-(benzonorbornen-2(_exo_)-yl bromobenzenesulfonate)tricarbonylchromium in 30 ml 70% acetone-water at 100° for 10 half-lives. Workup as above gave a yellow oil; nmr ($CDCl_3$) showed a ratio of uncomplexed to complexed aromatic region of 70/30; the complexed aromatic region bore some similarity to the starting sulfonate, but ten half-lives should have consumed all but 0.1% of the starting material; moreover, the absorption at 7.68 δ is a little downfield from the position of the starting sulfonate absorption. The complexed aromatic region resembles the superposition of the spectra of the _syn_-_exo_ and _anti_-_exo_ alcohols, and the analysis has been made on this premise; i.e., 70% benzonorbornen-2(_exo_)-ol, 15% _anti_-(benzonorbornen-2(_exo_)-ol)-tricarbonylchromium, and 15% _syn_-(benzonorbornen-2(_exo_)-ol)-tricarbonylchromium.

Similarly there was solvolyzed 56.6 mg anti-(benzonorbornen-2(endo)-yl bromobenzenesulfonate)tricarbonylchromium in 30 ml of 70% aqueous acetone at 105-120°. After about 2 half-lives, there was very little complex left (very little yellow color). The tube was removed from the bath at this point and the contents were worked up as above; nmr ($CDCl_3$) shows about 90% benzonorbornen-2(exo)-ol and 10% starting material.

Attempted Determination of pK_{R^+} Values for (Benzyl)tricarbonylmolybdenum and (Benzyl)tricarbonyltungsten Cations

(Benzyl)tricarbonylmolybdenum cation

Into a nitrogen-filled 5 cm UV cell, capped with a sealed stopper and containing a small stir bar, was injected about 15 ml degassed (freeze-thawed X 4) ethanol or aqueous sulfuric acid; then 6-7 µl of a solution comprised of 11.0 mg (benzyl methyl ether)tricarbonylmolybdenum in 0.70 ml degassed 95% ethanol was injected into the stirring solvent and the cell was quickly placed in the chamber of the spectrophotometer. The spectrum did not undergo any significant change from 95% ethanol to aqueous sulfuric acids.

(Benzyl)tricarbonyltungsten cation

Into a 5 cm UV cell filled with stirring ethanol or nitrogen-saturated aqueous sulfuric acid was injected 10-20 μl of a solution of 29.2 mg (benzyl methyl ether)-tricarbonyltungsten in 0.50 ml acetic acid. The cell was quickly placed in the chamber of the spectrophotometer and the absorption at 480 mμ was recorded as a function of time. The $p\underline{K}_{R^+}$ was determined as it was for the (benzyl)-tricarbonylchromium cation.

Infrared Technique

The carbonyl frequencies were measured as about 0.025 $\underline{M}$ solutions in chloroform, using the double beam mode of a Beckman IR 12 infrared spectrophotometer. The instrument was calibrated against polyethylene in the region under survey. The mid-point of the peak near its maximum intensity was taken as the absorption wavelength. The maximum uncertainty in the frequency value is estimated to be ± 1.0 cm^{-1}.

Nuclear Magnetic Resonance Technique

The solutions which were examined for the activation free energy values were about 0.2 molar in freshly distilled ethanol-free chloroform or in deuterochloroform which was obtained in small vials and therefore free of acidic traces which can result from long exposure to air.

The procedure followed for taking spectra at various temperatures was that one suggested in publication No. 87-100-110, Varian Associates, Palo Alto, California. Calibration of the dial setting was established with the Varian methyl alcohol and ethylene glycol standards. The actual temperature of the sample will be, according to page 3, publication No. 87-100-110, within 3° of the dial setting, after such calibration has been performed.

Tetramethyl silane was the internal standard.

The field strength was adjusted below that which just started to give saturation; the sweep speed was 250 seconds; sweep width was 100 cycles, amplitude 20-40. The coalescence temperature was obtained when the doublet just became a singlet with a flat top (46). At coalescence,

$$k = (\sqrt{2}/2) \times \pi \times (\delta_{AX}) \qquad (55)$$

where k is the rate constant for rotation at the coalescence temperature, and δ_{AX} is the width of the just coalesced line at its half height (46). The Eyring equation enables a calculation of ΔF^* from k at a given temperature, T; since we want the free energy of activation at the coalescence temperature, T_c.

$$\Delta F^*_{Tc} = 4.580 \times 10^{-3} \times T_c \times (9.976 + \log (T_c/\delta_{AX})) \qquad (56)$$

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