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# π-Complexed β-Arylalkyl Derivatives. 5. Polar Effects in the Formolysis of π-Complexed 9-Benzonorbornenyl and 9-Benzonorbornadienyl Methanesulfonates[1]


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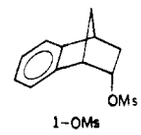
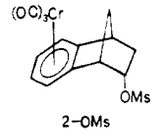
In a search for possible neighboring-group (direct d-orbital) participation by the metal, the formolysis rates of *anti*-9-benzonorbornenyl and *anti*-9-benzonorbornadienyl methanesulfonates (**6**- and **11**-OMs) have been compared with those of the π-complexed derivatives *endo*-tricarbonylchromium (**7**- and **12**-OMs), *exo*-tricarbonylchromium (**8**- and **13**-OMs) and, in the case of **6**-OMs only, the *endo*- and *exo*-trimethyl phosphite dicarbonylchromium derivatives (**9**- and **10**-OMs). At 60 °C the relative reactivities of **6**–**13**-OMs are 1.0, 0.005, 0.02, ~1.6, ~3.4, ~70, 0.06, and 0.07. All appear to yield unrearranged esters as the exclusive primary formolysis product, although formolysis of the complexes is accompanied by extensive oxidative decomplexation which prevents the determination of accurate titrimetric rate constants. It is suggested that the observed rate effects reflect differing ion-dipole interactions in the transition state of the rate-limiting step, rather than direct d-orbital participation by chromium.


In earlier papers in this series[2] we have reported several chromium tricarbonyl complexed β-arylalkyl methanesulfonates which solvolyze with partial or complete π-(aryl)-chromium tricarbonyl migration at rates that exceed those of their noncomplexed counterparts. To rationalize these and other observations, we suggested the possibility of direct d-orbital participation and/or σ–π homoconjugation. Each of these reaction paths, illustrated diagrammatically for the acetolysis of 2-[π-(phenyl)chromium tricarbonyl]-2-methyl-1-propyl methanesulfonate in Scheme I, suggests that the metal moiety should stabilize intermediates in which a positive charge is concentrated in the vicinity of the metal and requires that it precede the migrating aryl in a geometric sense during the rearrangement. We have shown that these conditions are fulfilled by demonstrating that at 75 °C the acetolysis of *exo*-2-[*endo*-π-(benzonorbornenyl)chromium tricarbonyl] methanesulfonate (**4**-OMs) is about 300 times as rapid as that of the exo-complexed methanesulfonate, **5**-OMs, that a portion of the former internally returns to the latter during acetolysis, and that both complexes yield the thermodynamically less stable endo-complexed *exo*-acetate, **4**-OAc, as the major product; cf. Scheme II.[3] We were able to demonstrate conclusively that tricarbonylchromium inductively retards acetolysis in cases where the aryl ring itself cannot participate anchimerically by comparing the acetolysis rate of *endo*-2-[*exo*-π-(norbornenyl)chromium tricarbonyl] methanesulfonate (**2**-OMs) with that of its noncomplexed analogue, **1**-OMs.[3] We were unable, however, to distinguish between direct metal bridging and σ–π homoconjugation as the mode of the metal-complex participation since either interpretation (Scheme I) appeared compatible with our data. In an effort to make such a distinction we have prepared and examined the solvolysis rates and products of a series of exo-π-complexed, *anti*-9-benzonorbornenyl and -norbornadienyl methanesulfonates designed to maximize the possibility of direct metal interaction.




1-OMs




2-OMs

## Results

**Preparation of Starting Materials.** The π-complexed, 9-substituted benzonorbornenyl and -norbornadienyl derivatives were prepared from the known[4] noncomplexed alcohols

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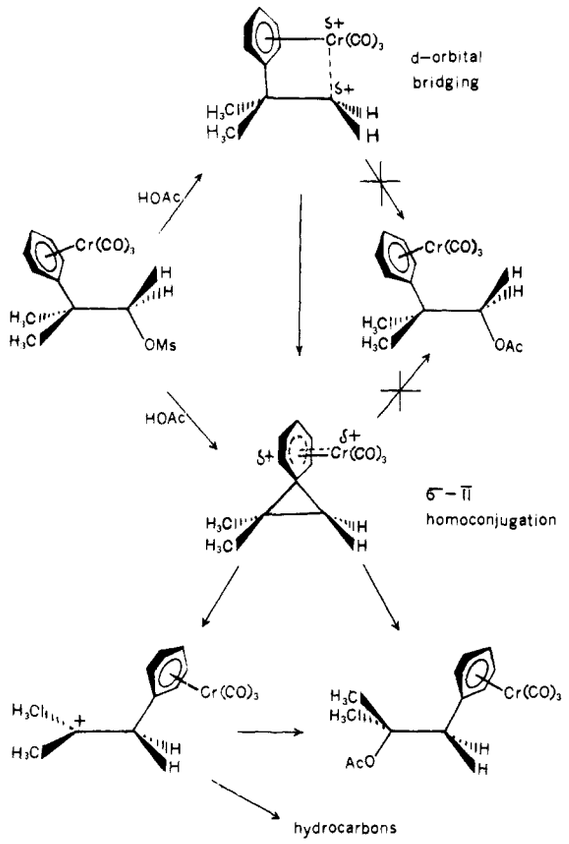
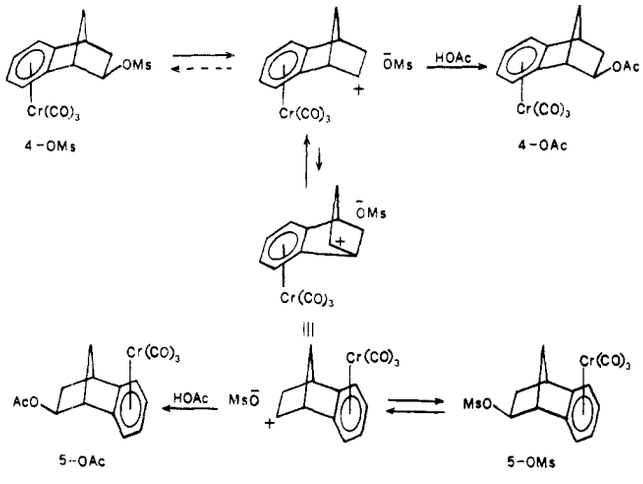
Scheme I. Possible Modes of Chromium Participation

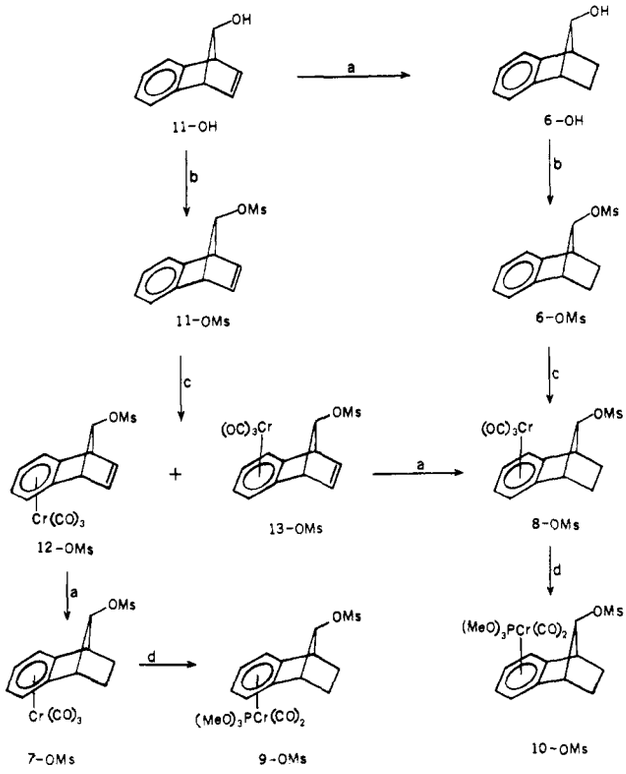



Scheme II. Stereochemistry of π-Arylchromium Tricarbonyl Migration




6- and 11-OH as outlined in Chart I. As indicated, the chromium tricarbonyl complexed benzonorbornadienyl methanesulfonates are most conveniently prepared by direct complexation of *anti*-9-benzonorbornadienyl methanesulfonate (**11-OMs**) with chromium hexacarbonyl in refluxing *n*-butyl ether–heptane. The resulting 60/40 mixture of *endo*- and *exo*-tricarbonylchromium derivatives, **12-** and **13-OMs**, respectively, can be separated by preparative thin-layer chromatography (TLC). While both **11-OH** and **11-OAc** can also be complexed in this manner,[5] the yields are lower, the resulting mixtures are more difficult to separate, and the complexes themselves appear to be less stable than their methanesulfonate counterparts. The use of more reactive complexing agents such as tris(acetonitrile)- or tris(pyridine)-chromium tricarbonyl[6] appears to offer no advantage either in convenience or yield. Since direct complexation of *anti*-

Chart I. Preparation of the π Complexes[a]

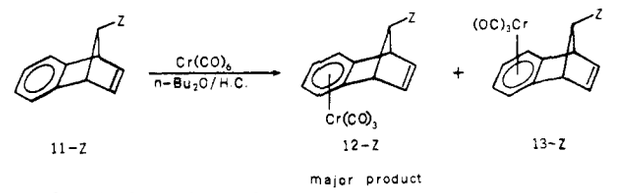



[a] a: $H_2$, Pd(C), EtOAc. b: MsCl, pyridine. c: $Cr(CO)_6$. d: $P(OMe)_3$, $C_6H_6$, $h\nu$.

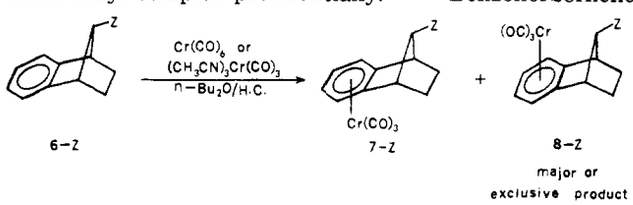
9-benzonorbornenyl alcohol (**6-OH**) or methanesulfonate (**6-OMs**) with chromium hexacarbonyl in *n*-butyl ether–heptane produces the corresponding exo complex exclusively, *anti*-9-[*endo*-π-(benzonorbornenyl)chromium tricarbonyl] methanesulfonate (**7-OMs**) is best prepared by catalytic hydrogenation of the endo-complexed norbornadienyl derivative, **12-OMs**; cf. Chart I.

The chromium trimethyl phosphite dicarbonyl complexes **9-** and **10-OMs** were prepared by photolysis of the chromium tricarbonyl complexes, **7-** and **8-OMs**, in the presence of excess trimethyl phosphite;[7] cf. Chart I. The phosphite complexes are markedly less stable than their tricarbonyl precursors and decompose extensively when preparative chromatography on active alumina or silica gel is attempted.

**Structure of the Complexes.** The stereochemistry of the metal moiety in each complex follows from its method of preparation and its proton magnetic resonance spectra. Except in cases where 9-substituted benzonorbornadienes form *exo*-chromium tetracarbonyl complexes,[5,8] direct complexation of benzonorbornadiene (**11-H**) (or its anti derivatives **11-Z**, Z = OH, OMs, or OAc) with chromium hexacarbonyl in




an ether–hydrocarbon solvent mixture gives the *endo*-π-arene tricarbonyl complex preferentially.[5,8a,9a] Benzonorbornene



(6-H)[9a] and its 2-[3,8a,9] and anti-9-substituted derivatives (3-Z and 6-Z, respectively, Z = OH, OMs, or OAc) complex predominantly or exclusively for the less hindered exo side.[5,8a]

The proton magnetic resonance spectra of exo- and endo-complexed benzonorbornenyl and -norbornadienyl derivatives exhibit characteristic differences which reflect the configuration of the metal moiety. The four aromatic hydrogens, which show the usual upfield shifts associated with the aromatic hydrogens of a π-(arene)chromium tricarbonyl,[10] appear as a complex AA'BB' or $A_2B_2$ pattern in the spectrum of each benzonorbornenyl or -norbornadienyl complex. In the spectrum of *exo*-2-[*exo*-π-(benzonorbornenyl)chromium tricarbonyl] acetate (5-OAc), whose structure is unequivocally known from the single-crystal x-ray diffraction studies of Amma et al.,[11] the chemical shifts of the A- and B-type protons differ by ~0.25 ppm while those of the endo complex, 4-OAc, differ by ~0.48 ppm. This characteristically greater difference in chemical shift is apparent in the proton spectra of all known endo-complexed benzonorbornenyl and -norbornadienyl derivatives;[3,5,8a,9] cf. Figure 1. As Wege and Wilkinson have noted,[5,8a] an additional feature of the proton spectra of exo-complexed 9-substituted benzonorbornenyl and -norbornadienyl derivatives which serves to differentiate them from those of their endo-complexed counterparts is the strong deshielding of the *syn*-9-hydrogen which is shifted 0.3–1.0 ppm downfield by the proximate tricarbonylchromium; cf. Figure 1. This effect is also evident, though less obvious, in the spectra of the 2-substituted benzonorbornenyl complexes.

**Solvolysis Products.** *anti*-9-Benzonorbornenyl brosylate (6-OBs) is reported to undergo acetolysis without rearrangement.[12] We find that the formolysis of 6-OMs also produces unrearranged product as do both the acetolysis and formolysis of *anti*-9-benzonorbornadienyl methanesulfonate (11-OMs).

Solvolyses of the complexes were conducted in the usual manner[2a,c] in buffered, deoxygenated acetic and formic acids. Where possible π-complexed products were isolated by crystallization or chromatographic techniques and identified by comparison of their infrared, NMR, and/or mass spectra. In cases where the instability of the complex or the small amount available precluded its isolation, the identity of a reaction product was inferred from a comparison of its TLC $R_f$ value with that of a known complex and by analysis of the organic material resulting from its oxidative decomplexation with ceric ammonium nitrate[2a] and, in some cases, subsequent reduction with lithium aluminum hydride.[2a] Product compositions where mixtures result were estimated from analytical TLC plates, from integrated NMR spectra of the mixture, and from gas chromatographic analysis of decomplexed reaction mixtures.[2a]

As best we have been able to determine, all of the chromium tricarbonyl complexed *anti*-9-benzonorbornenyl and -norbornadienyl methanesulfonates solvolyze in acetic and formic acids without rearrangement. The *anti*-9-[*endo*-π-(benzonorbornenyl)chromium trimethyl phosphite dicarbonyl] methanesulfonate (9-OMs) appears to yield the endo-complexed formate, 9-OCOH, exclusively when formolized for ~10 half-lives at 70 °C, although some decomplexation accompanies the reaction. The exo-complexed methanesulfonate, 10-OMs, under these conditions, yields the exo-complexed formate 10-OCOH predominantly but also produces about 10% of a noncomplexed formate of unknown structure. Since the relative amount of this latter product appears to increase with time, we doubt that it is a primary solvolysis product.

**Solvolysis Rates.** Titrimetric solvolysis rate constants for the noncomplexed methanesulfonates 6- and 11-OMs were determined in the usual manner.[2] Both give first-order plots which are linear through greater than 2 half-lives and titrimetric rate constants which are generally reproducible to within ±10%. Rate constants for the complexed methanesulfonates (cf. Table II) were determined in degassed solvents as described previously,[2a] the progress of the reaction being monitored by potentiometric titration.[2c] Most of these solvolyses, even in deoxygenated solvents, are accompanied by some oxidative decomplexation in the latter stages of the reaction as evidenced by the development of an orange to green color in the normally yellow solutions.[13] Decomplexation is so rapid at the higher temperatures required for the acetolyses of these relatively unreactive 9-substituted complexes that solvolysis constants for most of them could not be determined in this solvent.

Since the complexes solvolyze more rapidly in formic acid, lower temperatures can be utilized and approximate solvolysis rates can be established in this solvent. Even so, decomplexation during solvolysis is still a problem and the use of experimental infinity titers gives first-order plots which are far from linear, the rates appearing to decrease with time in a fairly regular manner. Since the complexes have been shown to solvolyze without rearrangement and are known to be pure initially, we rule out the usual possibilities of impure starting material and/or internal return to a less reactive methanesulfonate as the cause of this behavior and attribute it instead to decomplexation accompanying solvolysis.[13] because the first-order rate plots do not approach linearity at extended reaction times and since with but two exceptions the complexes are less reactive than their noncomplexed analogues, the nonlinearity of the first-order plots cannot be due simply to the presence of both complexed and noncomplexed methanesulfonates in the reaction mixture. Instead, it appears that the decomplexation actually produces formate ion[13] and, thus, causes the titrimetric formolysis rate of the complexed methanesulfonate to appear to decrease with time.

Since the extent of decomplexation during solvolysis varies irregularly from one run to another, the experimental titrimetric infinity values are meaningless as a basis for calculation of a solvolytic rate constant. In an effort to get some idea of the relative reactivity of the isomeric complexes, we utilize instead a hypothetical infinity titer adjusted to give the best fit of our data within an individual run to an assumed first-order rate law.[15] In this manner it is possible to produce highly linear first-order plots whose slopes are reproducible in duplicate runs to within about ±30%. While this method probably does not yield true formolysis rate constants—we suspect it underestimates them in most instances—we believe that it provides relative rate constants for isomeric complexes which are accurate to within at least an order of magnitude.

The apparent first-order titrimetric solvolysis constants and activation parameters for the noncomplexed 9-benzonorbornenyl and -norbornadienyl methanesulfonates are collected in Table I, while the relative rates of the complexes at 60 °C derived as described above are given in Table II.

## Discussion

Our kinetic data (Tables I and II) indicate that direct d-orbital participation by chromium is minimal in the solvolysis of *exo*-tricarbonylchromium complexed *anti*-9-benzonorbornenyl and -norbornadienyl methanesulfonates. In direct contrast to the effect of endo complexation which increases the acetolytic reactivity of *exo*-2-benzonorbornenyl methanesulfonate (4-OMs/3-OMs ≈ 1000/250 ≈ 4), exo complexation *decreases* the reactivity of the *anti*-9-benzonorbornenyl derivative [8-OMs/6-OMs ≈ 0.3 (HOAc); 8-OMs/6-OMs ≈ 0.02 (HCOOH)]. An even greater decrease is estimated in the benzonorbornadienyl case: 13-OMs/11-OMs ≈ 0.07/70 ≈ 0.001 (HCOOH). While it is true that in both the *anti*-9-benzonorbornenyl and -norbornadienyl series the *exo*-tricarbonylchromium complexes are formolytically slightly more reactive than their endo counterparts (8-OMs/7-OMs ≈

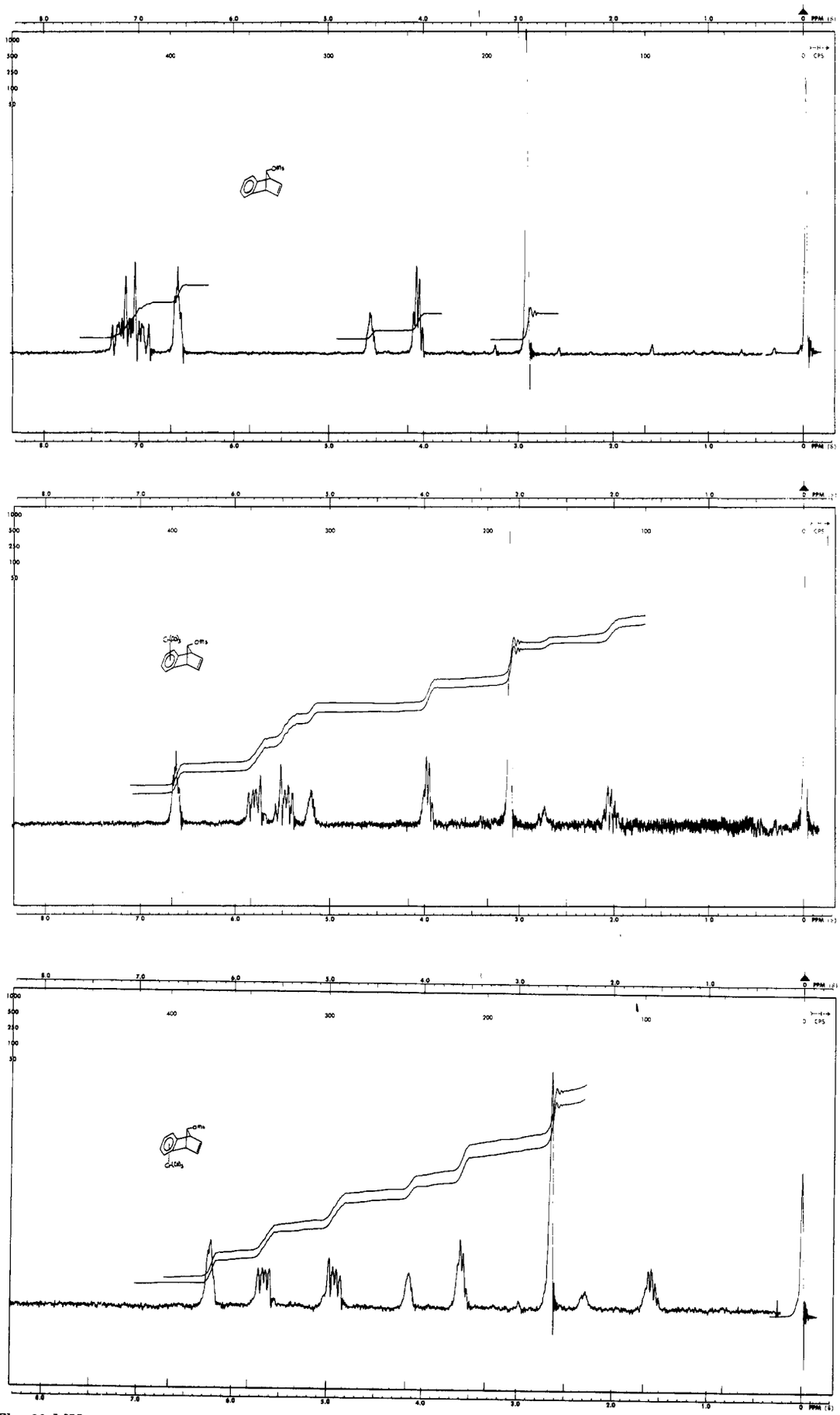


**Figure 1.** The 60-MHz proton magnetic resonance spectra of (upper) *anti*-9-benzonorbornadienyl methanesulfonate (**11**-OMs), (middle) *anti*-9-[*exo*-π-(benzonorbornadienyl)chromium tricarbonyl] methanesulfonate (**13**-OMs), and (lower) *anti*-9-[*endo*-π-(benzonorbornadienyl)chromium tricarbonyl] methanesulfonate (**12**-OMs).

**Table I. Apparent First-Order Solvolysis Constants and Activation Parameters for Noncomplexed Benzonorbornenyl and Benzonorbornadienyl Methanesulfonates**

| Compd[a] | Solvent | Temp, °C | $k$,[b] $s^{-1}$ | $\Delta H^*$, kcal/mol | $\Delta S^*$, eu |
|---|---|---|---|---|---|
| 1 | HOAc[c] | 60.0[d] | $1.69 \times 10^{-4}$ | 27.5 | −10.3 |
| 3 | HOAc[c] | 60.0[d] | $3.52 \times 10^{-8}$ | 24.0 | −3.9 |
| 6 | HOAc | 114.4 | $2.09 \pm 0.30 \times 10^{-4}$ | 26.6 | −7.1 |
| | | 97.7 | $4.97 \pm 0.26 \times 10^{-5}$ | | |
| | | 84.1 | $1.02 \pm 0.06 \times 10^{-5}$ | | |
| | | 60.0 | $6.68 \times 10^{-7}$ | | |
| 6 | HCOOH | 59.1 | $1.09 \times 10^{-3}$ | 25.5 | 4.3 |
| | | 59.0 | $1.03 \times 10^{-3}$ | | |
| | | 50.1 | $3.62 \pm 0.30 \times 10^{-4}$ | | |
| | | 40.0 | $9.58 \pm 1.17 \times 10^{-5}$ | | |
| | | 60.0 | $1.20 \times 10^{-3}$ | | |
| 11 | HOAc | 84.7 | $6.70 \pm 0.06 \times 10^{-4}$ | 25.8 | −1.1 |
| | | 84.3 | $7.93 \times 10^{-4}$ | | |
| | | 69.3 | $1.44 \pm 0.06 \times 10^{-4}$ | | |
| | | 60.1 | $3.89 \times 10^{-5}$ | | |
| | | 59.2 | $4.36 \pm 0.04 \times 10^{-5}$ | | |
| | | 60.0 | $4.61 \times 10^{-5}$ | | |

[a] Refer to Chart I for numbering; note that -OMs has been omitted for simplicity. [b] ± one standard deviation for replicate runs at the same temperature. [c] See ref 3 for raw data. [d] Estimated from data at other temperatures.

0.02/0.005 ≈ 4; **13**-OMs/**12**-OMs ≈ 0.07/0.06 ≈ 1.2), the consequence of having the chromium closer to the reactive site is much more pronounced in the *exo*-2-benzonorbornenyl case [**4**-OMs/**5**-OMs ≈ 1000/3 ≈ 330 (HOAc)].

The absence of an appreciable direct d-orbital interaction in the case of **8**-OMs may be due in part to the relatively large Cr–$C_9$ distance, ~3.6 Å—the Cr–$C_2$ distance in **4**-OMs is ~3.1 Å[11]—but this is probably not the whole story. The replacement of a strongly back-bonding carbonyl with a less strongly back-bonding trimethyl phosphite[16] should increase the electron density on chromium and render direct d-orbital participation more likely in **10**-OMs; yet, the effect of such a substitution is to increase substantially the formolytic reactivity of *both* the exo- *and* the endo-complexed *anti*-9-benzonorbornenyl derivatives: **10**-OMs/**8**-OMs ≈ 3.4/0.02 ≈ 170; **9**-OMs/**7**-OMs ≈ 1.6/0.005 ≈ 320. Thus, while **10**-OMs is actually slightly more reactive than *anti*-9-benzonorbornenyl methanesulfonate itself (**10**-OMs/**6**-OMs ≈ 3.4), it would appear incorrect to attribute this effect to direct d-orbital participation since it is also evident in the endo complex, **9**-OMs/**6**-OMs ≈ 1.6, where such interaction is not possible.

If a difference in the extent of direct d-orbital participation is not the cause of the changes in solvolytic rate which result when a carbonyl ligand is replaced by trimethyl phosphite, what is? Each of the π-complexed *anti*-9-benzonorbornenyl and -norbornadienyl derivatives solvolyses without significant rearrangement; hence, σ–π homoconjugation is an unlikely possibility. Because the partial bond moments associated with the ligand-to-metal bonds in some π-arene and π-cyclopentadienyl complexes can be appreciable,[16] it occurred to us that the formolytic rate enhancements which we observe in going from a tricarbonyl to a dicarbonyl trimethyl phosphite complex might be due to differences in the electrostatic interactions between the ligand-to-metal dipole and the developing charge at $C_9$. Since the unusual geometry of the π complexes precludes the use of σ-bound substituents to mimic the dipolar effect of the metal ligands, we have utilized a modified Kirkwood–Westheimer treatment[18] to estimate whether rate effects of the magnitude which we observe could possibly be due to electrostatic interactions alone. The results of such calculations, carried out as described in the Experimental Section, may be compared with the observed rate ratios; cf. Table III.

Apparently the substantial rate enhancements observed upon going from tricarbonylchromium to trimethyl phosphite dicarbonylchromium complexes of comparable geometry *could* derive, from electrostatic effects alone![19]

This possibly fortuitous congruity of theory and experiment raises some interesting questions. Could similar electrostatic interactions determine the relative reactivities of other benzonorbornenyl derivatives (cf. Table II)? Is the demonstrated tendency of tricarbonylchromium to precede the ring of a migrating π-complexed aryl,[3] in fact, a manifestation of such electrostatic effects rather than the consequence of either σ–π homoconjugation or d-orbital bridging?[20] We do not presently have answers to these questions but are hopeful that studies now in progress may provide them.

The introduction of an additional double bond into the benzonorbornenyl ring results in a more reactive anti-9 methanesulfonate: thus, **11**-OMs/**6**-OMs = 69 (HOAc, 60 °C). The acetolysis of **6**-OBs, which is $10^5$ times more facile than that of 7-norbornyl brosylate,[12] is thought to occur with π-arene participation via a symmetric transition state.[12] The additional anchimeric effect of the double bond in **11**-OMs in the absence of σ delocalization[21] (no rearranged products) may be a consequence of laticyclic type participation similar to that observed in the solvolysis of 7-norbornadienyl derivatives.[22] It is reasonable to expect the additional double bond to shift π-electron density toward the arene as it does in benzocyclobutadiene[23] for benzonorbornadiene may be thought of as a weakly coupled bis(homobenzocyclobutadiene).[24]

In the light of this conjecture it is of interest to note that π complexation apparently decreases the solvolytic reactivity of *anti*-9-benzonorbornadienyl methanesulfonate (**11**-OMs) to a much greater extent than it does the benzonorbornenyl analogue, **6**-OMs: vis., **12**-OMs/**11**-OMs ≈ 0.06/70 ≈ 0.0009; **13**-OMs/**11**-OMs ≈ 0.07/70 ≈ 0.001. Apparently, by utilizing the aromatic π MOs that would normally interact weakly with the isolated double bond, the more strongly bound tricarbonylchromium is able to obliterate all bis(homobenzocyclobutadiene)-like character and, hence, any laticyclic stabilization of the intermediate cation by the isolated double bond.

## Experimental Section[25]

**Preparation of the Methanesulfonates.** In the manner of Veazey,[2a] the appropriate alcohol was allowed to react with methanesulfonyl chloride in cold, dry pyridine. The reaction mixtures were maintained at −10 °C for 2 days prior to workup.

**Preparation of *anti*-9-Benzonorbornadienyl Methanesulfonate (11-OMs).** A white crystalline solid (mp 92–94 °C) was obtained from **11**-OH[4] in 94% yield: IR ($CHCl_3$) 3075, 3025, 2940, 1470 (CH), 1380, 1350, 1173 $cm^{-1}$ (–$OSO_2$–); NMR ($CDCl_3$) δ 7.10 (m, 4 H, aromatic), 6.70 (m, 2 H, olefinic), 4.59 (m, 1 H, syn C-9), 4.08 (m, 2 H, bridgehead C-1 and C-4), 2.93 (s, 3 H, $CH_3SO_2$–) (cf. Figure 1). Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12; O, 20.31; S, 13.57. Found: C, 61.03; H, 5.03; O, 20.18; S, 13.76.

**Preparation of *anti*-9-Benzonorbornenyl Methanesulfonate (6-OMs).** White needles obtained from **6**-OH[4] were purified by recrystallization from ether–pentane in an overall yield of 74%: mp 53–55 °C; IR ($CCl_4$) 3040, 3018, 2970, 2950, 2900, 2868, (CH), 1470 (–$CH_2$), 1460 (–$CH_3$), 1163, 1182 (–$SO_2$–), 886, 864, 830, 816 $cm^{-1}$ (S–O); NMR ($CDCl_3$) δ 7.14 (s, 4 H, aromatic), 4.42 (m, 1 H, syn C-9), 3.42 (m, 2 H, bridgehead C-1 and C-4), 3.00 (s, 3 H, –$SO_2CH_3$), 2.17 (m, 2 H, endo C-2 and C-3), 1.23 (distorted q, 2 H, exo C-2 and C-3). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92; O, 20.14; S, 13.46. Found: C, 60.37; H, 5.81; O, 20.42; S, 13.20.

**Preparation of *anti*-9-Benzonorbornadienyl Acetate (11-OAc).** Employing the general procedure of Winstein and Trifan,[26] **11**-OH[4] was acetylated with acetic anhydride in glacial acetic acid at 75 °C. Distillation afforded a clear, oily liquid: bp 81–84 °C (0.3 mm); IR ($CHCl_3$) 3075, 3020, 3005 (CH), 1745 (C=O), 1220, 1038 (C–O), 698 $cm^{-1}$ (cis olefin); NMR ($CDCl_3$) δ 7.05 (m, 4 H, aromatic), 6.55

**Table II. Approximate Relative Solvolysis Rates of Benzonorbornenyl and Benzonorbornadienyl Methanesulfonates at 60 °C**

| Compd | Registry no. | Solvent | Rel rate | Compd | Registry no. | Solvent | Rel rate |
|---|---|---|---|---|---|---|---|
| 6 | | HOAc | 1.00 | 6 | 64425-80-5 | HCOOH | 1.00 |
| 1 | 31351-15-2 | HOAc[a] | 0.053 | 7 | 64440-61-5 | HCOOH | 0.005 |
| 2 | 33220-89-2 | HOAc[b] | <0.004 | 8 | 64519-53-5 | HCOOH | 0.02 |
| 3 | 31351-14-1 | HOAc[a] | 250 | 9 | 64475-08-7 | HCOOH | ~1.6 |
| 4 | 33218-83-6 | HOAc[b] | >1000 | 10 | 64440-64-8 | HCOOH | ~3.4 |
| 5 | 33247-11-9 | HOAc[b] | 3 | 11 | 64425-79-2 | HCOOH | (69)[c] |
| 8 | | HOAc | ~0.3 | 12 | 64440-60-4 | HCOOH | 0.06 |
| 11 | | HOAc | 69 | 13 | 64519-52-4 | HCOOH | 0.07 |

[a] See Table I; note that -OMs has been omitted for simplicity. [b] Estimated from data in ref 3. [c] Estimated from the relative acetolysis rates of 11 and 6.

**Table III. Formolysis Rate Ratios of Isogeometric Trimethyl Phosphite Dicarbonyl- and Tricarbonylchromium π-Arene Complexes**

| | Obsd[a] | Predicted[b] |
|---|---|---|
| 9-OMs/7-OMs | ~300 | ~100 |
| 10-OMs/8-OMs | ~200 | ~300 |

[a] Estimated from the relative formolysis rates at 60 °C; cf. Table II. [b] Calculated from the electrostatic model at 60 °C; cf. Experimental Section and Table IV.

(m, 2 H, olefinic), 4.85 (m, 1 H, syn C-9), 3.95 (m, 2 H, bridgehead C-1 and C-4), 1.96 (s, 3 H, $CH_3CO_2$–). These spectra are in reasonable agreement with the reported literature values.[4]

**Preparation of *anti*-9-Benzonorbornenyl Acetate (6-OAc).** When the general acetylation procedure of Winstein and Trifan[26] was employed, 6-OH was converted to 6-OAc, a colorless liquid [bp 81–84 °C (0.25 mm)] in 86% yield: IR ($CHCl_3$) 3050, 2975, 2955, 2910, 2875 (CH), 1750 (C=O), 1490 (–$CH_2$–), 1480, 1395, 1380 (–$CH_3$), 1228, 1113, 1042 (C–O), 912 $cm^{-1}$ (aromatic);[4] NMR ($CDCl_3$) δ 7.09 (m, 4 H, aromatic), 4.52 (br s, 1 H, syn C-9), 3.28 (m, 2 H, bridgehead C-1 and C-4), 2.1–1.9 (m, 2 H, endo C-2 and C-3) superimposed on a singlet at 1.98 (3 H, $CH_3CO_2$–), 1.13 (distorted q, 2 H, exo C-1 and C-4). The above spectra are in good agreement with published values.[4]

**Preparation of *anti*-9-Benzonorbornadienyl Formate (11-OCOH).** Solvolysis of 1.00 g (4.23 mmol) of 11-OMs in 50 mL of 0.10 M sodium formate in formic acid afforded the desired product in greater than 90% yield. GLC of the crude reaction mixture showed only one product: bp 115–118 °C (oil bath) (0.8 mm); IR ($CHCl_3$) 3067, 3007, 3002, 2940 (CH), 1750 (C=O), 1487, 1482, 1332 (–$CH_2$–), 1230, 1182, 1155 (C–O), 704 $cm^{-1}$ (cis olefin); NMR ($CDCl_3$) δ 7.86 (s, 1 H, –OCOH), 7.08 (m, 4 H, aromatic), 6.55 (m, 2 H, olefinic), 4.77 (m, 1 H, syn C-9), 3.98 (m, 2 H, bridgehead C-1 and C-4). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41; O, 17.19. Found: C, 77.26; H, 5.40; O, 17.34.

**Preparation of *anti*-9-Benzonorbornenyl Formate (6-OCOH).** Catalytic hydrogenation at atmospheric pressure of 11-OCOH with 10% Pd/C in ethyl acetate afforded the desired formate in greater than 90% yield: bp 79 °C (0.45 mm); IR ($CHCl_3$) 3005, 2975, 2950, 2880 (–CH–), 1745 (C=O), 1495, 1485 (–$CH_2$–), 1212, 1190, 1110 $cm^{-1}$ (C–O); NMR ($CDCl_3$) δ 7.94 (s, 1 H, –OCOH), 7.10 (s, 4 H, aromatic), 4.60 (m, 1 H, syn C-9), 3.32 (m, 2 H, bridgehead C-1 and C-4), 2.03 (m, 2 H, endo C-2 and C-3), 1.14 (distorted q, 2 H, exo C-2 and C-3). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; O, 17.00. Found: C, 76.46; H, 6.56; O, 16.97.

**Preparation of the Tricarbonylchromium π-Complexed Compounds.** All tricarbonylchromium complexes were prepared in a Strohmeier apparatus[27] using the general procedure of Veazey.[2a] Optimum yields were obtained when reaction mixtures, saturated with inert gas, were allowed to reflux for about 24 h. The samples were purified by recrystallization from benzene–ether–pentane mixtures.

**Preparation of *anti*-9-[*exo*-π-(Benzonorbornenyl)chromium tricarbonyl] Methanesulfonate (8-OMs).** Reaction of 6-OMs yielded the desired yellow, crystalline complex in 65% yield. TLC (eluent: ether–pentane, 75:25) indicated a single isomer ($R_f$ 0.75): mp 151–153 °C dec; IR ($CHCl_3$) 3015, 2950 (CH), 2030, 1955 (C≡O), 1390, 1370, 1208, 1173 (–$SO_2$–), 668, 636, 538 $cm^{-1}$ (Cr–C); NMR ($CDCl_3$) δ 5.75 and 5.45 (m, 4 H, aromatic), 4.70 (m, 1 H, syn C-9), 3.28 (perturbed q, 2 H, bridgehead C-1 and C-4), 3.19 (s, 3 H, $CH_3SO_2$–), 2.18 (m, 2 H, endo C-2 and C-3), 1.36 (perturbed q, $J$ = 4 Hz, 2 H, exo C-2 and C-3). Anal. Calcd for $C_{15}H_{14}O_6CrS$: C, 48.13; H, 3.77; O, 25.65; S, 8.57; Cr, 13.89. Found: C, 48.21; H, 3.95; O, 25.47; Cr, 13.97.

**Preparation of *anti*-9-[*exo*-π-(Benzonorbornadienyl)chromium tricarbonyl] Methanesulfonate (13-OMs).** Reaction of 11-OMs produced a yellow, microcrystalline complex in 62% yield. TLC of the solid [eluent: ether–pentane, 80:20 (0.5 mm)] revealed the presence of two complexes ($R_f$ 0.20 and 0.30) in a 60/40 ratio. Separation of these two products was effected by preparative TLC in the absence of light. A typical run utilized about 250 mg of the mixture in 1 mL of acetone on a TLC plate (20 × 40 cm) which had been coated with silica gel (PF-254, ca. 2 mm) and conditioned for 2.5 h at 120 °C.

Elution of this plate was accomplished in a sandwich developing chamber fitted for continuous elution using an ether–pentane solution (75:25). Following the separation of the two isomers, the eluent was removed, and with the aid of a UV lamp, the yellow bands were scraped from the plate. Extraction of the separated bands from silica gel with acetone afforded yellow solutions which when concentrated and diluted with pentane at −10 °C yielded yellow crystalline precipitates. Spectral analysis of the yellow needles isolated from the TLC band of shorter retention time ($R_f$ 0.30) indicated them to be the desired *exo*-tricarbonylchromium isomer 13-OMs: mp 179 °C dec; 25% yield; IR ($CHCl_3$) 3010 (CH), 1990, 1920 (C≡O), 1400, 1210 (–$SO_2$–), 670, 635 $cm^{-1}$ (Cr–C); NMR ($CD_3COCD_3$) δ 6.63 (m, 2 H, olefinic), 5.80 and 5.56 (m, 4 H, aromatic), 5.20 (m, 1 H, syn C-9), 3.89 (m, 2 H, bridgehead C-1 and C-4), 3.09 (s, 3 H, $CH_3SO_2$–) (cf. Figure 1); parent ion at *m/e* 372. Anal. Calcd for $C_{15}H_{12}O_6CrS$: C, 48.39; H, 3.25; O, 25.78; Cr, 13.97; S, 8.61. Found: C, 48.25; H, 3.26; O, 25.36; S, 8.41.

**Preparation of *anti*-9-[*endo*-π-(Benzonorbornadienyl)-chromium tricarbonyl] Methanesulfonate (12-OMs).** This complex, a component of the isomeric mixture obtained from the Strohmeier complexation of 11-OMs, was isolated via preparative TLC (vide supra) from the band of lower $R_f$ value in about 30% yield. Analytical TLC indicated an isomer distribution of 12-OMs/13-OMs in the crude reaction mixture of ca. 60/40. The *endo*-tricarbonylchromium isomer exhibits the following properties: mp 167–170 °C dec; IR ($CHCl_3$) 3020 (CH), 1988, 1910 (C≡O), 1390, 1370, 1200, 1171 (–$SO_2$–), 706 (cis olefin), 669, 634 $cm^{-1}$ (Cr–C); NMR ($CD_3COCD_3$) δ 6.63 (m, 2 H, olefinic), 6.06 and 5.32 (m, 4 H, aromatic), 4.54 (m, 1 H, syn C-9), 3.99 (distorted q, 2 H, bridgehead C-1 and C-4) (cf. Figure 1), 3.04 (s, 3 H, $CH_3SO_2$–); parent ion *m/e* 372. Anal. Calcd for $C_{15}H_{12}O_6CrS$: C, 48.39; H, 3.25; O, 25.78; Cr, 13.97; S, 8.61. Found: C, 48.25; H, 3.24; O, 25.52; S, 8.45.

**Preparation of *anti*-9-[*endo*-π-(Benzonorbornenyl)chromium tricarbonyl] Methanesulfonate (7-OMs).** Catalytic hydrogenation of 12-OMs at atmospheric pressure employing 10% Pd/C in ethyl acetate required several days at 55 °C. The yield of the desired complex was about 60%. The endo complex of the saturated methanesulfonate, 7-OMs, exhibits the following properties: mp 152–154 °C; IR ($CHCl_3$) 3010, 2955 (CH), 1985, 1908 (C≡O), 1480 (–$CH_2$–), 1395, 1375, 1208, 1172 (–$SO_2$–), 669, 638 $cm^{-1}$ (Cr–C); NMR ($CDCl_3$) δ 5.52 and 5.13 (m, 4 H, aromatic), 437 (m, 1 H, syn C-9), 3.19 (distorted q, 2 H, bridgehead C-1 and C-4), 3.00 (s, 3 H, $CH_3SO_2$–), 2.21 (m, 2 H, endo C-2 and C-3), 1.72 (distorted q, 2 H, exo C-2 and C-3); parent ion at *m/e* 374. Anal. Calcd for $C_{15}H_{14}O_6CrS$: C, 48.13; H, 3.77; O, 25.65; Cr, 13.89; S, 8.57. Found: C, 48.33; H, 3.71; O, 25.33; S, 8.74.

**Preparation of *anti*-9-[*exo*-π-(Benzonorbornenyl)chromium dicarbonyl trimethyl phosphite] Methanesulfonate (10-OMs).** Following the general procedure for photolytic ligand substitution first developed by Strohmeier,[10c,28] an inert gas saturated benzene

solution of 8-OMs containing excess trimethyl phosphite was irradiated in a Pyrex vessel for 2–3 h employing a 250-W sunlamp. The water-washed and magnesium sulfate dried, yellow-orange solution was concentrated to ca. 20 mL, and crystallization was initiated by the addition of pentane at 0 °C. TLC (eluent benzene) of the resulting yellow-orange crystals revealed one major component ($R_f$ 0.16) along with several minor ones. Recrystallization afforded pure **10**-OMs in 64% yield: mp 132–134 °C; IR ($CHCl_3$) 3010, 2990, 2950, 2840 (CH), 1915, 1860 (C≡O), 1390, 1360, 1205, 1172 (–$SO_2$–), 1015 (C–O), 710 (P–C), 652, 624 $cm^{-1}$ (Cr–C); NMR ($CD_3COCD_3$) $\delta$ 5.12 (m, 4 H, aromatic), 4.88 (m, 1 H, syn C-9), 3.60 and 3.49 [d, $J_{CP}$ = 11 Hz, 9 H, $P(OCH_3)_3$], 3.14 (s, 3 H, $CH_3SO_2$–) superimposed on a multiplet at 3.10 (2 H, bridgehead C-1 and C-4), 2.08 (m, 2 H, endo C-2 and C-3), 1.30 (distorted q, 2 H, exo C-2 and C-3). Anal. Calcd for $C_{17}H_{23}O_8CrPS$: C, 43.41; H, 4.93; O, 27.21; Cr, 11.05; P, 6.58; S, 6.82. Found: C, 43.58; H, 4.94; P, 6.52; S, 6.72.

**Preparation of *anti*-9-[*endo*-π-(Benzonorbornenyl)chromium dicarbonyl trimethyl phosphite] Methanesulfonate (9-OMs).** Employing the same procedure outlined for the preparation of **10**-OMs (vide supra), **7**-OMs was converted to the desired trimethyl phosphite derivative in 52% yield: mp 115–116 °C; IR ($CHCl_3$) 2990, 2945, 2840 (CH), 1910, 1855 (C≡O), 1390, 1370, 1172 (–$SO_2$–), 1016 (C–O), 653, 624 $cm^{-1}$ (Cr–C); NMR ($CDCl_3$) $\delta$ 5.20 and 4.83 (m, 4 H, aromatic), 4.36 (m, 1 H, syn C-9), 3.62 and 3.41 [d, $J$ = 12 Hz, 9 H, $P(OCH_3)_3$], 3.19 (m, 2 H, bridgehead C-1 and C-4), 3.02 (s, 3 H, $CH_3SO_2$–), 2.06 and 1.91 (m, 4 H, exo/endo C-2 and C-3). Anal. Calcd for $C_{17}H_{23}O_8CrPS$: C, 43.41; H, 4.93; O, 27.21; Cr, 11.05; P, 6.58; S, 6.82. Found: C, 43.51; H, 4.72; P, 6.44; S, 6.92.

**Preparation of *exo*-π-(Benzonorbornene)chromium Dicarbonyl Trimethyl Phosphite (10-H).** Irradiation of a benzene solution of 8-H[8a,9a] containing excess trimethyl phosphite yields the desired monosubstitution product, an orange-yellow oil, in 48% yield: IR ($CHCl_3$) 3015, 2980, 2950, 2875, 2845 (CH), 1905, 1850 (C≡O), 1380, 1368 ($CH_2$, $CH_3$), 1205, 1030 (P–O), 660, 622 $cm^{-1}$ (Cr–C); NMR ($CDCl_3$) $\delta$ 5.05 and 4.83 (m, 4 H, aromatic), 3.62 and 3.43 [d, $J_{CP}$ = 11 Hz, 9 H, $P(OCH_3)_3$], 3.02 (m, 2 H, bridgehead C-1 and C-4), 1.95 (m, 4 H, endo C-2 and C-3 plus syn and anti C-9), 1.23 (m, 2 H, exo C-2 and C-3). Anal. Calcd for $C_{16}H_{21}O_5CrP$: C, 51.07; H, 5.63; O, 21.26; Cr, 13.82; P, 8.23. Found: C, 51.01; H, 5.23; Cr, 13.65; P, 8.39.

**Acetolysis Product Studies of Noncomplexed Methanesulfonates.** In a typical run 10 mL of acetic acid, which was about 0.20 M in methanesulfonate and 0.30 M in sodium acetate, was sealed in a large test tube and heated in a thermostated oil bath at a temperature used for the rate study. After 10 half-lives, the tube was cooled and opened, and its contents was poured over ice water. The mixture was extracted with ether. The ether extract was washed sequentially with 10% sodium carbonate and water, dried over sodium sulfate, and concentrated to produce the expected acetate in ca. 90% yield.

The purity and structure of the sole product detected by GLC was established by comparison of its IR and NMR spectra with authentic samples of **6**- or **11**-OAc.

**Acetolysis Product Study of *anti*-9-[*exo*-π-(Benzonorbornenyl)chromium tricarbonyl] Methanesulfonate (8-OMs).** Under an inert atmosphere, 0.074 g (0.20 mmol) of **8**-OMs was added to 15 mL of a solution of 0.0505 M sodium acetate in deoxygenated anhydrous acetic acid. This yellow solution was sealed in an ampule under nitrogen and heated for 9.5 half-lives at 98 °C. The cool, orange-brown solution, which turned green when exposed to air, was poured over 75 mL of crushed ice and extracted with four 50-mL portions of ether–pentane. The combined extracts were washed with a 10% sodium carbonate solution and with water. A TLC check of this solution (Kodak plates, ether–pentane 80:20) revealed the presence of only one complex ($R_f$ 0.34, ether–pentane 70:30), whose retention time was less than that of the starting material, **8**-OMs. To the slightly yellow extract was added, with stirring, 5 mL of a saturated solution of ceric ammonium nitrate in acetone.[2a] The resultant mixture was washed three times with cold water and dried over anhydrous magnesium sulfate. After concentration to ca. 10 mL, a molar excess of lithium aluminum hydride was added. The etheral mixture was allowed to reflux overnight and worked up by addition of water and 2 N sulfuric acid, followed by extraction with three 50-mL portions of ether–pentane (50:50). After washing with a 10% sodium carbonate solution and with water, the product was dried over anhydrous magnesium sulfate. The IR of the sole component detected and collected by GLC (85% yield by internal standard) is identical with that of authentic **6**-OH.

**Formolysis Product Studies of Noncomplexed Methanesulfonates.** As with the acetolysis product studies, 10-mL samples of a buffered formic acid solution ca. 0.02 M in **6**- or **11**-OMs were solvolyzed. In each case the IR and NMR of the sole product, detected by GLC and collected by distillation (90% yield), are consistent with those expected of **6**- or **11**-OCOH, respectively.

**Formolysis Product Studies of Chromium Tricarbonyl Complexed Methanesulfonates.** The same general procedure outlined for the acetolysis product studies of π complexes was employed, except that, because of the small amount of material available, the complexes were run in pairs of equimolar mixtures: **7**- and **8**-OMs or **12**- and **13**-OMs. In each case a TLC run prior to oxidative decomplexation with ceric ammonium nitrate indicated the presence of two complexed products in approximately equal amounts. The tricarbonyl complexed products from **7**- and **8**-OMs were found to have $R_f$ values of 0.51 and 0.66 (ether–pentane, 80:20), respectively; those from **12**- and **13**-OMs had $R_f$ values of 0.51 and 0.63 (ether–pentane, 80:20), respectively. The overall yield of unrearranged alcohol—**6**-OH from **7**- and **8**-OMs, **11**-OH from **12**- and **13**-OMs—isolated by GLC following ceric oxidation and hydride reduction was 75% in each case by GLC with an internal standard. The identity of the noncomplexed alcohol was established in each case by comparison of the IR and NMR spectra of a collected sample with those of the known compound.

**Formolysis Product Study of Chromium Dicarbonyl Trimethyl Phosphite Complexed Methanesulfonates.** The formolysis of equimolar mixtures of the trimethyl phosphite complexes **9**- and **10**-OMs was carried out in the manner described previously for the tricarbonyl complexes. In each case TLC analyses of the crude formolysis mixtures indicate the presence of approximately equal amounts of two π-complexed products, $R_f$ 0.22 and 0.32 (benzene), presumed to be the endo- and exo-complexed formates **9**- and **10**-OCOH. A GLC analysis following ceric oxidation of the product mixtures indicated the presence of two noncomplexed components, whose ratio appeared to depend upon the reaction time. The overall yield of decomplexed products, determined gas chromatographically using an internal standard, was ~75% in all runs. The major decomplexed product (that of longer retention time) was collected and found to be identical with authentic *anti*-9-benzonorbornenyl formate (**6**-OCOH). The second component (that of shorter retention time) could not be characterized except by its IR and mass spectrum which indicated a formate ester with a molecular ion of *m/e* 192.

To obtain an accurate ratio of these two noncomplexed products, a 30-mL formolysis sample, ca. 0.02 M in **10**-OMs, was placed in a thermostated bath at 70 °C. Aliquots (10 mL) were withdrawn at 5, 10, and 15 half-lives and examined by GLC following oxidative decomplexation with ceric ammonium nitrate. The ratio of the unknown product relative to **6**-OCOH varied with time, being 0.11 at 5 half-lives, 0.15 at 10 half-lives, and 0.16 at 15 half-lives, implying that the unknown ester is not a primary formolysis product. Because of the small amount of material available, we were unable to determine whether it is also produced in the formolysis of **9**-OMs.

**Kinetic Studies and Data Treatment.** Acetolysis and formolysis rates on the noncomplexed methanesulfonates were determined titrimetrically as described previously.[2c] For the complexed derivatives acetolysis and/or formolysis rates were obtained from potentiometric titrations of ~0.02 M solutions of the methanesulfonates in degassed, buffered acetic or formic acid. Degassed rate solvents were prepared by passing dry, oxygen-free nitrogen through them for 10–20 min at 70–80 °C and then allowing them to cool under the same inert atmosphere. All rate-sample preparations were carried out in a glovebag under a nitrogen atmosphere. In a typical run, the appropriate amount of complex was weighed into a 10-mL volumetric flask, and this flask, along with the open rate tubes, was placed in a glovebag. All of the apparatus was flushed with a stream of dry nitrogen, the glovebag was closed, and the rate solution was prepared in the following manner. The well-mixed solution was pipetted in slightly greater than 1-mL quantities into each rate tube. These tubes were flushed with a stream of $N_2$, corked, removed from the glovebag, cooled in ice water, and sealed as quickly as possible. The sealed tubes were placed in a thermostated oil bath (±0.05 °C) and removed at regular intervals. After cooling, the rate tubes were opened, and a 1-mL aliquot of solution was removed, placed in a titration vessel, and diluted with 5 mL of glacial acetic acid. Titration was accomplished with a perchloric–acetic acid solution using a Radiometer-Copenhagen pH stat–autoburette combination.[25]

Because of the oxidative decomplexation which accompanies the solvolyses of the complexed methanesulfonates,[13] titrimetric infinity titers obtained in this manner are of limited utility for the calculation of the rate constants for individual runs. Instead, the curved first-order plots were adjusted to give the best straight lines (assuming first-order kinetics) by varying the "infinity titer" until the coefficient of determination of the least-squares linear regression line through the experimental points was maximized. A FORTRAN IV computer program derived originally from that of Wiberg[15] was used to ac-

**Table IV. Parameters for the Charge-Dipole Calculation**

| Compd | $\mu^a$ | $\theta$, deg | $R$, Å |
|---|---|---|---|
| 7-OMs | 0.6 | 1.95 | 5.06 |
| 8-OMs | 0.6 | 13.8 | 4.49 |
| 9-OMs | 3.2 | 1.81 | 5.29 |
| 10-OMs | 3.2 | 13.2 | 4.71 |

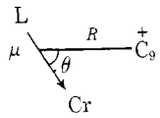
[a] In debyes directed toward chromium.

complish this. In every case the coefficient of determination of an individual run exceeded 0.98. In almost all cases the "rate constant" derived in this manner was considerably greater than that which would have resulted had the experimental infinity titer been utilized. Rate constants of replicate runs were generally reproducible to within ±30%, and the activation parameters computed in the usual manner[29] from replicate runs at three or more temperatures had standard deviations that did not exceed 0.25 kcal/mol in the case of $\Delta H^*$ or 0.7 eu in the case of $\Delta S^*$. These approximate activation parameters were used to estimate the *relative* solvolysis rates of the individual complexes at 60 °C (Table II).

**Charge-Dipole Calculations.** To estimate the effect of changes in the magnitude and direction of a ligand dipole, e.g., the substitution of a trimethyl phosphite for a carbonyl, upon the relative solvolysis rate of a complexed methanesulfonate, we have assumed a point-dipole model[18d] similar to that originally developed by Westheimer[18a] and modified by Stock.[18b] This calculation utilizes the equation[18b]

$$\log (k_2/k_1) = (e/2.3kTD_E)\left[\left(\frac{\mu \cos\theta}{R^2}\right)_2 - \left(\frac{\mu \cos\theta}{R^2}\right)_1\right]$$

and requires values of the bond moments of the Cr–CO ($\mu_1$) and Cr–P(OMe)$_3$ ($\mu_2$) bonds, the angles, $\theta_1$ and $\theta_2$, which these moments make with respect to a line joining their midpoints with $C_9$ (the site of developing positive charge), the distances from the midpoint of the Cr–CO and Cr–P(OMe)$_3$ bonds from $C_9$, $R_1$ and $R_2$, respectively, and an estimate of the effective dielectric constant $D_E$.




For purposes of this calculation we used values of the bond moments suggested by Strohmeier et al. ($\mu_1 \approx 0.6$ D,[17b] $\mu_2 \approx 3.2$ D),[17d] directed toward the metal in each case, and ligand-to-chromium bond lengths of 1.85 (Cr–CO)[11b] and 2.31 Å (Cr–P).[30] The required angles ($\theta$) and distances ($R$) were derived from the single-crystal x-ray data of Amma et al.[11b] on *exo*-2-[*exo*-π-(benzonorbornenyl)chromium tricarbonyl] acetate (**5**-OAc) by assuming that the atomic coordinates of all the carbons which make up the bicyclic framework of the π-complexed *anti*-9-benzonorbornenyl methanesulfonates are identical with those of the corresponding carbons in **5**-OAc, that trimethyl phosphite, being a more bulky ligand, replaces the carbonyl which lies in the plane defined by $C_9$, Cr, and the center of the aromatic ring, and that the atomic coordinates of the endo-complexed metal moieties may be derived from those of the exo by reflection of the latter in the plane of the aromatic ring. The resulting parameter values are summarized in Table IV.

The substitution of these values, together with an assumed effective dielectric constant, $D_E$, of 2[18d] into the defining equation, permits estimates to be made of the relative solvolysis rates at 60 °C of **9**- and **7**-OMs and of **10**- and **8**-OMs; cf. Table III. If the effective dielectric constant is actually greater than 2, then, of course, the predicted rate ratios are smaller.

**Registry No.**—**6**-OH, 1198-20-5; **6**-OCOH, 64425-81-6; **6**-OAc, 1207-28-9; **8**-H, 64440-62-6; **10**-H, 64457-61-0; **11**-OCOH, 64425-82-7; **11**-OAc, 16031-35-9; **11**-OH, 6991-42-0; trimethyl phosphite, 121-45-9.

## References and Notes


(1) (a) Portions of this work have been reported at the 25th Southeastern Regional Meeting of the American Chemical Society, Charleston, S.C., Nov 1973, Abstract No. 395, and (b) the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept 1976, Abstract ORGN 055.
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(13) We suspect that the decomposition of a π-(arene)chromium tricarbonyl complex in anhydrous acetic (R = $CH_3$) or formic (R = H) acid in the absence of oxygen produces the red, octahedral, diamagnetic carboxylato-bridged dinuclear Cr(II) derivative,[14] viz., 2Cr(0) + 6RCOOH → $Cr_2(O_2CR)_4(RCOOH)_2$ + 4RCOO$^-$ + 2H$_2$, which, when exposed to oxygen, is rapidly oxidized to a mononuclear, hexacoordinate Cr(III) species: 2Cr(II) + O$_2$ + 2RCOOH → 2Cr(III) + 2H$_2$O + 2RCOO$^-$.
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(19) We attach no particular significance to the fact that the calculations predict a larger rate enhancement in the exo complex, whereas the observed ratio (Table II) appears larger in the endo; both ratios are clearly approximate; either could change substantially with further refinement.
(20) Cf. R. S. Bly, K-K. Tse, and R. K. Bly, *J. Organometal. Chem.*, **117**, 35 (1976).
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(25) Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, West Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrometer, Model 337, Varian A-60 or XL-100-15 NMR spectrometers using tetramethylsilane as an internal standard, and a Hitachi Perkin-Elmer RMU-6 single-focusing mass spectrometer. Vapor-phase gas chromatographic analyses utilized F & M Model 500 or Varian Model 1800 gas chromatographs equipped with 6 or 10 ft × 0.25 in. copper columns packed with 5–15% Carbowax 20M on 60–90 mesh Chromosorb W, helium being used as a carrier gas at flow rates of 100–120 mL/min. For preparative thin-layer chromatography silica gel (E. Merck, PF-254 with $CaSO_4$ binder, Brinkman Instruments, Inc.) was employed. Eastman Chromagram precoated silica gel sheets were used for analytical TLC. Potentiometric titrations were accomplished on a Radiometer-Copenhagen system composed of an Autoburette Model ABU1b, a Titrator Model TTT1C, and a titragraph Model SBR2C.
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