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(46) This result is consistent with our earlier observation on the $[Mo(CO)_5]$ intermediate afforded thermally from $Mo(CO)_5NHC_5H_{10}$,[8] as well as observations in the matrix photochemistry of group 6B hexacarbonyl species.[21]
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Metal-Stabilized Carbonium Ions Derived from Bis(tricarbonylchromium) Complexes of Diarylmethanes[1]

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Abstract: (π,π'-Diarylcarbinol)bis(tricarbonylchromium) complexes, prepared either by direct reaction of a diarylcarbinol with chromium hexacarbonyl or by reduction of the appropriate (π,π'-diaryl ketone)bis(tricarbonylchromium) with sodium borohydride, react with $HPF_6/(EtCO)_2O$ to give the respective very stable (π,π'-diarylcarbonium hexafluorophosphate)bis(tricarbonylchromium) complexes. These blue carbonium ion salt complexes are carbon electrophiles which alkylate alcohols, primary and secondary amines, and highly nucleophilic aromatic and heterocyclic compounds such as *N,N*-dimethylaniline, pyrrole, and *N*-methylpyrrole. A ^{13}C NMR study of the (π,π'-di-*p*-tolylcarbonium chlorostannate)bis(tricarbonylchromium) complex in dichloromethane solution, as well as an IR study, provided evidence of extensive delocalization of positive charge from carbon to chromium in these carbonium ion complexes.

Introduction

There has been much interest in carbonium ions which are stabilized by π-ligand complexes of transition metals.[2] Ferrocenyl-substituted carbonium ions, I, have been studied most extensively,[2,3] but other systems, II,[4] III,[5] IV,[6] V,[8] and VI,[7] also have been investigated. During a study of the electronic effects of the $Cr(CO)_3$ group on arene ligands, Holmes, Jones, and Pettit attempted the synthesis of a stable π-complexed carbonium ion salt of type VII.[9] Treatment of (π-benzyl alcohol)tricarbonylchromium with perchloric or tetrafluo-

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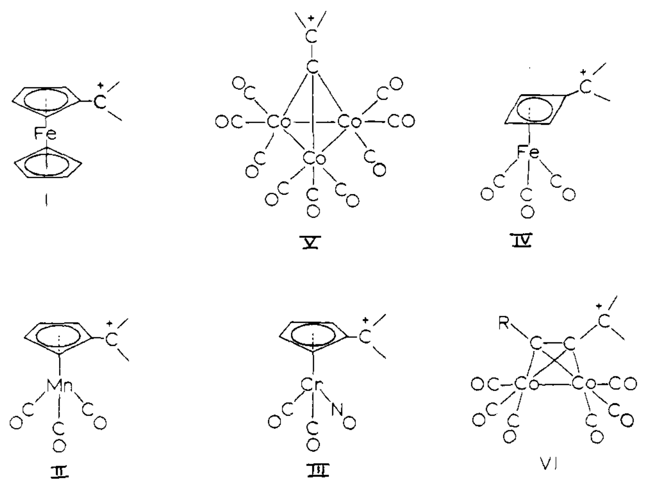
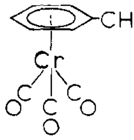
METAL STABILIZED CARBONIUM IONS



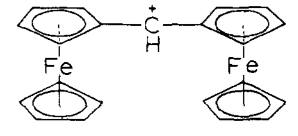
roboric acids in acetic anhydride medium resulted in a rapid decomposition reaction in which carbon monoxide was evolved; no stable salts of VII could be isolated. Similar decomposition



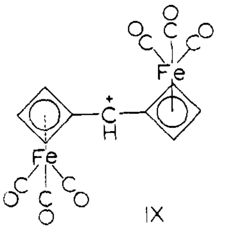
VII

was encountered when (π-benzyl chloride)tricarbonylchromium was treated with $AgClO_4$, $AgBF_4$, or $SbCl_5$ in nitromethane. Even attempts to form stable cationic species using complexes in which the ligand was known to form stable carbonium ions when it was not complexed gave decomposition with liberation of carbon monoxide. These results were rationalized in terms of effects which would weaken the metal carbonyl system, and an explanation in terms of the absence of any stabilization of VII due to the presence of the metal substituent was rejected. Indeed, Holmes et al. found that the rate of solvolysis of (π-benzyl chloride)tricarbonylchromium was greater than that of uncomplexed benzyl chloride by a factor of ~10^5 and that solvolysis of (π-benzhydryl chloride)-tricarbonylchromium was ~10^3 times faster than solvolysis of uncomplexed benzhydryl chloride. This was clear evidence that the $Cr(CO)_3$ substituent did, in fact, stabilize carbonium ions of type VII to a considerable extent. However, the rate of solvolysis of α-chlorocumene was accelerated only by a factor of 28 when it had been converted to its tricarbonylchromium complex.[10] This suggests that steric effects become important in the stabilization of such chromium-complexed tertiary carbonium ions. Trahanovsky and Wells[11] determined the pK_{R^+} value for cation VII in concentrated sulfuric acid to be -11.8. For the uncomplexed benzyl cation, $pK_{R^+} < -17.3$,[12] so coordination to $Cr(CO)_3$ does result in thermodynamic stabilization. The value of $pK_{R^+} = -11.8$ implies that the stabilization of VII is not as great as that of the ferrocenylmethyl cation, $C_5H_5FeC_5H_4CH_2^+$, whose pK_{R^+} value is -1.28,[13] but it does compare favorably with pK_{R^+} values for other relatively stable, wholly organic carbonium ions, such as Ph_3C^+ ($pK_{R^+} = -6.6$) and Ph_2CH^+ ($pK_{R^+} = -13.4$).[14]

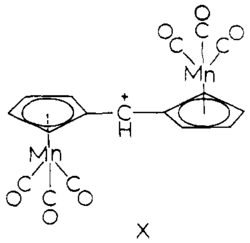
It had been found that the carbonium ion salts containing two ferrocenyl (VIII),[15] two tricarbonylironcyclobutadiene (IX),[16] or two tricarbonylmanganesecyclopentadienyl (X)[17] substituents are much more stable than those containing only one of these substituents. Thus one would expect that the presence of *two* tricarbonylchromiumarene substituents on a carbonium ion center might result in a system of sufficient kinetic and thermodynamic stability to allow the isolation of stable salts of type XI.[31] Several examples of dinuclear complexes of arenes with chromium tricarbonyl groups are known,[19] and they generally are quite stable and more resistant to oxidation than their mononuclear analogues.



VIII



IX

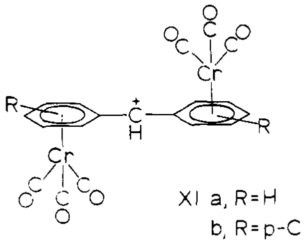


X

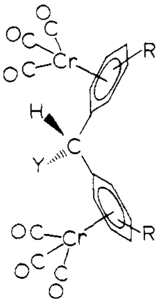
We report here concerning the preparation and properties of such carbonium ions derived from bis(tricarbonylchromium) complexes of diarylmethanes.

Results and Discussion

In order to generate a carbonium ion of type XI, a starting material, XII, was required, with a suitable leaving group, Y,



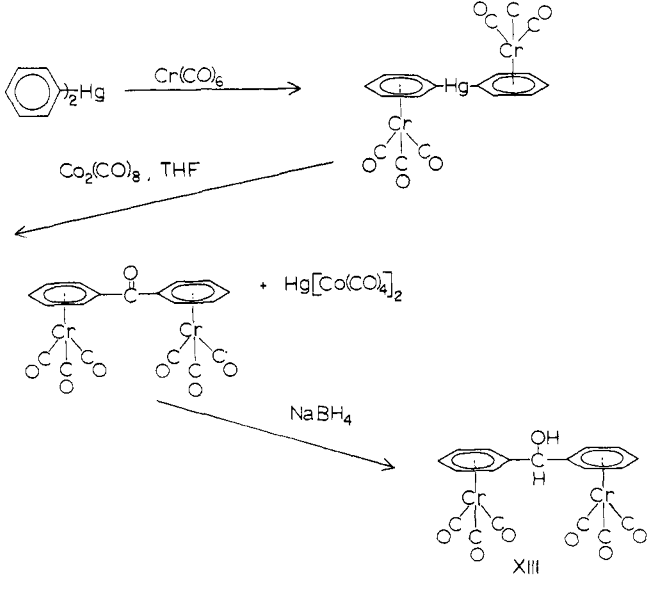
XI a, R=H
b, R=p-CH$_3$



XII

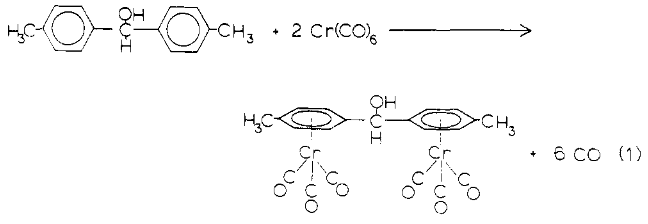
either OH, halogen, tosylate, etc. The benzhydrol derivative, XIII, initially was prepared by the reaction sequence shown in Scheme I. The preparation of the required (π,π'-diphenylmercury)bis(tricarbonylchromium) had been reported by

Scheme I



Razuvaev et al. in 1972,[20] and the synthesis of diaryl ketones by reaction of diarylmercurials with dicobalt octacarbonyl had been developed in these laboratories.[21] The red-orange (π,π'-benzophenone)bis(tricarbonylchromium) was very stable and only moderately soluble in polar organic solvents. Reduction of this ketone with sodium borohydride in methanol gave yellow (π,π'-benzhydrol)bis(tricarbonylchromium) in high yield. A reaction sequence similar to that shown in Scheme I served in the preparation of (π,π'-di-*m*-tolylcarbinol)bis(tricarbonylchromium), starting from di-*m*-tolylmercury.

While this three-step procedure did give the desired alcohols, it was time consuming and cumbersome. Therefore, the direct reaction of a diarylcarbinol with chromium hexacarbonyl was examined. Di-*p*-tolylcarbinol was found to react with 2 molar equiv of chromium hexacarbonyl in refluxing diglyme/*n*-octane to give, after a reaction time of 18 h, the desired (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium) (XIV) in 46% yield (eq 1). In similar fashion, a reaction of di-*p*-tolylcarbinol with 2 molar equiv of $(H_3N)_3Cr(CO)_3$ in refluxing dioxane (4 h reaction time) gave this alcohol complex in 47% yield. No attempts were made to optimize yields.

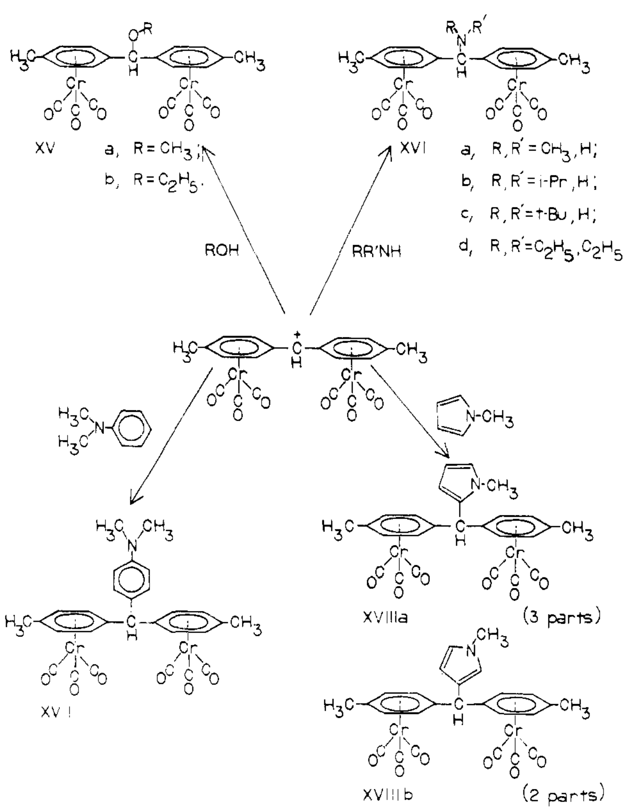


XIV

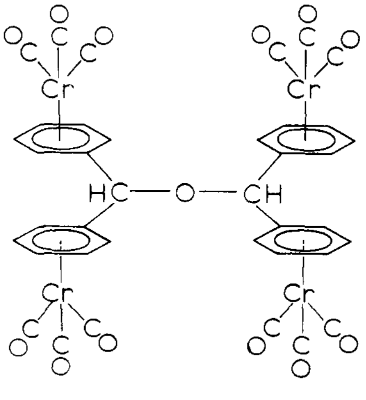
The availability of the required alcohols allowed investigation of the derived carbonium ions. Treatment of a slurry of (π,π'-benzhydrol)bis(tricarbonylchromium) in propionic anhydride with a solution of 65% aqueous hexafluorophosphoric acid in propionic anhydride, under nitrogen, resulted in precipitation of a royal-blue solid. Such a blue solid also was obtained by similar treatment of (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium) with HPF_6 in propionic anhydride.

The chemical conversions of these blue solids, studied more extensively in the case of the (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium)-derived product (Scheme II), are consistent with their formulation as the desired carbonium ion salts, XIa and XIb, with PF_6^- counterion. In general, when a slurry of the blue carbonium ion salt in benzene was treated with a nucleophile (ethanol, *tert*-butylamine, etc.), the color changed immediately to yellow, and a homogeneous solution resulted. Hydrolysis and subseqeunt workup of the organic phase generally gave the expected product in good yield. Such reactions proceeded readily with methanol and ethanol to give the respective ether, but the carbonium ion salt XIb did not react with *tert*-butyl alcohol, presumably because the latter is too hindered. Reactions with primary and secondary amines gave the expected secondary and tertiary amines. Both carbonium ions alkylated very reactive aromatic nucleophiles, such as *N,N*-dimethylaniline, pyrrole, and *N*-methylpyrrole, but they did not react with anisole and less nucleophilic benzene derivatives. Attempted reaction of XIb hexafluorophosphate with ferrocene, also a very reactive aromatic nucleophile, resulted in destruction of both reactants, possibly as a result of a redox process of unknown nature.

Scheme II

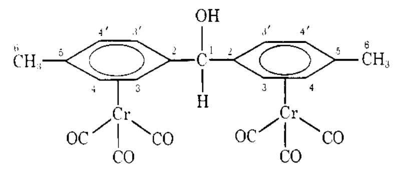


Our initial attempts to study the spectroscopic properties of these (π,π'-diarylcarbinol)bis(tricarbonylchromium)-derived carbonium ions were unsuccessful.[1] The ^{13}C NMR spectra of the parent alcohols were readily obtainable. However, the hexafluorophosphate and tetrafluoroborate salts of cations XIa and XIb were found to be insoluble in common organic solvents such as chloroform and dichloromethane and to react with *N,N*-dimethylformamide, acetonitrile, and nitromethane. Neither carbonium ion was stable in concentrated sulfuric acid. Thus, when alcohol XIII was added to frozen, degassed concentrated sulfuric acid, and the mixture was allowed to warm slowly, the solution became blue as the solid began to dissolve. However, the color eventually changed to red, and carbon monoxide was evolved. A green solution finally was formed, and when this solution was poured onto ice, the starting alcohol, XIII, was not regenerated. Neat trifluoroacetic acid has been used as a solvent and proton source in the generation of metal-stabilized carbonium ions. When alcohol XIII was added to frozen, degassed trifluoroacetic acid, the mixture became blue. However, a homogeneous solution was not formed, and filtration gave a light blue solution from which a yellow solid separated after it had stood for 2 h under nitrogen. The latter was identified as the ether XIX, which was produced by reaction of carbocation XIa with unconverted alcohol. Supporting this explanation was the observation that the infrared spectrum of the solution obtained when alcohol XIV was dissolved in neat trifluoroacetic acid exhibited bands due to both the cationic species XIb as well as the starting al-

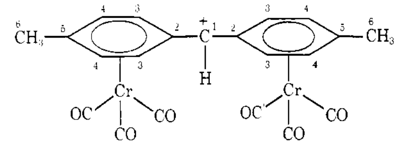


XIX

Table I. Proton-Decoupled ^{13}C Nuclear Magnetic Resonance Spectra of (π,π'-Di-*p*-tolylcarbinol)bis(tricarbonylchromium) and Its Derived Carbonium Ion in Dichloromethane Solution



Carbon no.	δ_C, ppm (±0.2 ppm)
1	73.0
2	112.3
3,3′	95.4, 94.1
4,4′	93.1, 92.9
5	111.2
6	21.5
CO	234.3



1	141.4
2	117.1
3	97.8
4	96.4
5	117.1
6	21.9
CO	230.8

cohol. It would seem that trifluoroacetic acid is not a sufficiently strong acid to completely ionize alcohols XIII and XIV. The action of $BF_3{\cdot}OEt_2$ on XIV forms the carbonium ion to a greater extent, but bands due to the alcohol were still evident in an infrared spectrum of its solution in $BF_3{\cdot}OEt_2$. Solutions of cation XIb suitable for ^{13}C and IR spectroscopic studies could be obtained by treatment of a dichloromethane solution of alcohol XIV with an excess of tin(IV) chloride. Although a blue solid precipitated when $SnCl_4$ was added to a solution of XIV in dichloromethane, enough carbonium ion salt, with $SnCl_4OH^-$ or, more probably, $SnCl_5^-$ counterion, remained in solution to allow spectroscopic studies to be carried out at −20 °C. (Decomposition occurred at higher temperature.)

The proton-decoupled ^{13}C NMR spectra of alcohol XIV and of the derived carbonium ion XIb, both obtained in dichloromethane solution, are recorded in Table I. As noted above, (π,π'-di-*m*-tolylcarbinol)bis(tricarbonylchromium) also had been prepared. However, its proton-decoupled ^{13}C NMR spectrum was much more complex than that of the isomeric alcohol XIV. Presumably, the presence of the *m*-methyl substituents, in addition to the restricted rotation about the methinyl-to-ring carbon bonds, results in the presence of several stereoisomers in solution. For this reason, further work was carried out with XIV instead.

The assignments of the resonances in the proton-decoupled ^{13}C NMR spectrum of alcohol XIV are straightforward and are based on chemical shifts and splittings observed in an off-resonance decoupling experiment. The assignments of the resonances in the spectrum of the carbonium ion XIb are not as certain since an off-resonance proton-decoupled spectrum could not be obtained in a reasonable amount of time. The assignments shown in Table I are based on the following considerations.

The fewer number of lines in the carbonium ion spectrum can be explained in terms of hindered rotation in the case of the alcohol. In the latter, the two arenetricarbonylchromium groups are attached to an sp^3-hybridized carbon atom. A molecular model of this compound shows that the two groups are locked into a configuration which makes carbon atom 3 distinct from 3′ and carbon atom 4 distinct from 4′. In the carbonium ion, the arenetricarbonylchromium groups are attached to a formally sp^2 center with planar geometry, which would allow for freer rotation. Thus carbon atoms 3 and 3′ and carbon atoms 4 and 4′ would become identical. Carbon atoms 2 and 5 in alcohol XIV have very similar chemical shifts, so it is not unreasonable to accept that they would have coincidental chemical shifts in the carbonium ion. Furthermore, with the exception of carbon atom 1, the carbonium ion carbon resonances should be in positions similar (~ ±5 ppm) to those of the same carbon atoms in the precursor alcohol, assuming that the trends hold in this case which were found to obtain in the case of other metal-stabilized carbonium ions for which comparisons with the parent alcohols are available.

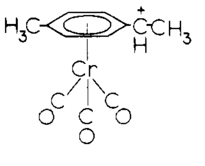
While the $\Delta\delta_C$ values for carbon atoms 2, 3, 4, 5, and 6 and those for the carbon monoxide ligands on going from the alcohol to the carbonium ion are small, ranging from 2.4 to 5.9 ppm, this $\Delta\delta_C$ value for the methinyl carbon atom (C-1) is 68.4 ppm, with the carbonium ion carbon atom being deshielded with respect to C-1 in the alcohol. This downfield shift is relatively small, compared to wholly organic carbonium ion systems in which a high degree of resonance stabilization of the positive charge is not possible (e.g., $\Delta\delta_C$ for $Me_2CHOH \rightarrow Me_2CH^+ = 255.7$ ppm).

Presently prevailing opinion seems to be that the charge density at a carbonium ion center is the major factor governing its shielding.[22] Thus, as a first approximation, one might rationalize this small $\Delta\delta$ value in terms of more extensive charge delocalization in the present arenechromium system. However, ^{13}C chemical shifts depend not only on the charge density at a carbon atom, but also on hybridization and on anisotropic, diamagnetic, and paramagnetic effects,[23] so such a direct correlation between ^{13}C shieldings and charge distribution may not obtain. In any case, such small $\Delta\delta$ values are characteristic of highly stabilized transition metal substituted carbonium ions (e.g., $(OC)_9Co_3CCHPhOH \rightarrow (OC)_9Co_3CCHPh^+$, $\Delta\delta = -35.7$ ppm;[8b] $(C_5H_5)Fe(C_5H_4CHPhOH) \rightarrow (C_5H_5)Fe(C_5H_4CHPh)^+$, $\Delta\delta = -49.4$ ppm;[24] and $(OC)_3Fe(C_4H_3CHPhOH) \rightarrow (OC)_3Fe(C_4H_3CHPh)^+$, $\Delta\delta = -70.1$ ppm[6b]), and we and others have taken these to be indicative of the high degree of stabilization of these species as indicated by other chemical and physical evidence. However, in view of the uncertainties mentioned above, the stabilities of the carbonium ions within this class most certainly should not be ranked on the basis of these numbers.

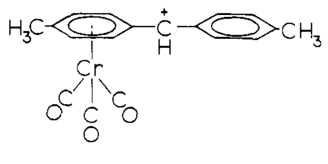
In all of these transition metal stabilized carbonium ion systems the available evidence suggests that the positive charge accumulates to a large measure on the metal, although the details of how and to what extent this occurs are still in dispute. In some cases, IR spectroscopic evidence may be cited in support of this view, including the present organochromium systems. (π,π'-Di-*p*-tolylcarbinol)bis(tricarbonylchromium) exhibits terminal CO stretching frequencies at 1965 and 1890 cm^{-1} (A_1 and E modes, respectively) of similar intensity, with the E band being broader, as expected for local C_{3v} symmetry. When the cation XIb is formed by the action of $SnCl_4$ on the alcohol in dichloromethane, shifts to higher energy (ν(CO) 2030 w and 1980 s, broad, cm^{-1}) occur with concomitant change in local symmetry of the molecule. Such blue shifts (65 and 90 cm^{-1}, respectively) are indicative of an accumulation of positive charge on the metal.[32] This would result in diminished back-donation from the metal to CO antibonding orbitals and hence in an increase of CO bond order and the CO stretching frequency. The upfield shift of the CO ^{13}C shielding of the alcohol XIV when cation XIb is formed from it is in agreement with this picture.

The chemical reactivity of cation XIb also supports the view developed above, in which the positive charge initially generated at C-1 upon ionization of the alcohol accumulates at the metal atoms. The species thus formed, with only a fractional positive charge at C-1, should be a rather unreactive and very selective carbon electrophile. The fact that it will alkylate *N,N*-dimethylaniline but not anisole and less nucleophilic aromatics can be accommodated readily into this picture. However, carbonium ion XIb is by no means as stabilized, hence as deactivated chemically, as the diferrocenylcarbonium ion VIII, whose perchlorate salt was reported to decompose only slowly in alcohols[15a] and whose tetrafluoroborate salt could be recrystallized and recovered unchanged from methanol.[15b]

In conclusion, we note that during the course of this study, Italian workers[26] reported the generation of the $(OC)_3Cr$-stabilized carbonium ions XX and XXI from the respective alcohols. These species were sufficiently stable in fluorosulfonic acid medium at −60 °C to allow their ^1H NMR spectra to be recorded. A later paper by the same group[27] reported a ^{13}C NMR study of the complexed carbocations XX and XXI and of the alcohols from which they were derived. The values of $\Delta\delta$ for the alcohol/XX and alcohol/XXI systems were 59.1 and 64.3 ppm, respectively. On the basis of the ^1H and ^{13}C NMR data, it was concluded that in these systems also a considerable portion of the charge is transferred to the metal.



XX



XXI

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen in flame-dried glassware using rigorously dried solvents. Thin layer chromatography was used to assess the purity of products (Eastman Chromagram Sheet No. 6063, alumina). All compounds were bright yellow or orange and could be observed without further visualization. Since all reactions yielded single products, full-scale column chromatography was not required. New compounds were purified by recrystallization.

Infrared spectra were obtained using a Perkin-Elmer 457A double-beam grating infrared spectrophotometer. Spectra were obtained in either chloroform or carbon tetrachloride solution using sodium chloride cavity cells with a path length of 0.1 mm. ^1H NMR spectra were recorded on either a Varian Associates T60 or a Hitachi Perkin-Elmer R-20B spectrometer. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane. Melting points are uncorrected.

Starting Materials. Chromium hexacarbonyl (Strem Chemical Co.) and 65% hexafluorophosphoric acid (Alfa/Ventron) were used as received. Propionic anhydride was distilled at reduced pressure and stored under nitrogen over molecular sieves. Nucleophilic substrates were distilled prior to use. Di-*p*-tolylcarbinol was prepared by the reaction of *p*-tolylmagnesium bromide and *p*-tolualdehyde and was recrystallized from hexane prior to use, mp 68–69 °C (lit.[28] mp 69 °C).

Preparation of (π,π'-Diarylmercury)bis(tricarbonylchromium) Complexes. (1) (π,π'-Di-*m*-tolylmercury)bis(tricarbonylchromium). This preparation is based on the procedure of Razuvaev et al.[20]

A 1-L, three-necked flask, equipped with a reflux condenser topped with a no-air stopper through which was placed a syringe needle as a nitrogen inlet and a long copper wire, was flame dried, flushed with nitrogen, and charged with 15.28 g (40 mmol) of di-*m*-tolylmercury, 17.60 g (80 mmol) of chromium hexacarbonyl, 150 mL of *n*-octane, and 125 mL of diglyme (distilled from sodium benzophenone ketyl, bp 64–65 °C at 25 Torr). The mixture was heated at reflux for 11 h. During this time, occasional scraping of the condenser inside walls with the copper wire was necessary in order to return sublimed $Cr(CO)_6$ to the reaction flask. The yellow reaction mixture was allowed to cool to room temperature. It then was filtered and the residue was washed with acetone until the washings were colorless. The combined filtrate and washings were evaporated at reduced pressure. The oily, yellow residue was crystallized from chloroform/hexane to give 13.28 g (51%) of the title complex, mp 200 °C dec. Anal. Calcd for $C_{20}H_{14}O_6Cr_2Hg$: C, 36.71; H, 2.36. Found: C, 36.68; H, 2.15. NMR (Me_2SO-d_6): δ 2.11 (s, 6 H, ring CH_3) and 5.30–6.00 ppm (m, 8 H, Ph). IR (acetone): ν(CO) 1958, 1875 cm^{-1}.

(2) (π,π'-Diphenylmercury)bis(tricarbonylchromium). A similar procedure was used in the preparation of this complex in 52% yield. Its IR spectrum (in acetone, ν(CO) 1963, 1886 cm^{-1}) was in agreement with that reported.[20]

Preparation of (π,π'-Benzophenone)bis(tricarbonylchromium) and (π,π'-3,3′-Dimethylbenzophenone)bis(tricarbonylchromium). A 500-mL, three-necked, round-bottomed flask equipped with a nitrogen inlet and a mechanical stirring unit was flushed with nitrogen and flame dried and then was charged with 9.3 g (27 mmol) of $Co_2(CO)_8$, 8.0 g (12.2 mmol) of (π,π'-di-*m*-tolylmercury)bis(tricarbonylchromium), and 200 mL of dry THF. The mixture was stirred under nitrogen at room temperature for 24 h. The dark orange reaction mixture then was treated with 50 mL of saturated aqueous sodium sulfide to convert the $Hg[Co(CO)_4]_2$ produced to insoluble mercuric sulfide. The mixture was filtered through Celite and the filter cake was washed with THF until the washings were colorless. The combined filtrate and washings were evaporated at reduced pressure, leaving an orange-red residue which was dissolved in a small amount of chloroform. Filtration chromatography (silicic acid, chloroform eluent) gave a red-orange solution which was evaporated at reduced pressure to leave an orange-red solid which was chromatographed on a silicic acid column (benzene eluent). After a small yellow band (starting material) had been eluted an orange-red band followed. This material was obtained by evaporation of the benzene solution as a red oil. The latter could be crystallized from methanol to give 3.85 g of red needles, mp 255–256 °C. The yield of the product, (π,π'-3,3′-dimethylbenzophenone)bis(tricarbonylchromium), was 66%, based on the mercurial. Anal. Calcd for $C_{21}H_{14}O_7Cr_2$: C, 52.29; H, 2.93. Found: C, 52.76; H, 3.07. NMR ($CDCl_3$): δ 2.30 (s, 6 H, CH_3) and 5.25–6.08 ppm (m, 8 H, phenyl H). IR (CCl_4): ν(CO) 1983, 1920 (ketone C=O), 1649 cm^{-1}.

(π,π'-Benzophenone)bis(tricarbonylchromium) was prepared in similar manner from 23.1 mmol of $Co_2(CO)_8$ and 12.9 mmol of (π,π'-diphenylmercury)bis(tricarbonylchromium) in 250 mL of THF in 43% yield: red-orange needles, mp 164–165 °C dec. Anal. Calcd for $C_{19}H_{10}O_7Cr_2$: C, 50.23; H, 2.22. Found: C, 49.79; H, 2.33. IR ($CHCl_3$): ν(CO) 1998, 1983, 1971, 1912 cm^{-1}; ketone C=O, 1640 cm^{-1}.

Reduction of the Ketones. A 125-mL Erlenmeyer flask was charged with a slurry of 0.33 g (0.7 mmol) of (π,π'-benzophenone)bis(tricarbonylchromium) and 40 mL of methanol. The orange slurry was cooled in an ice bath and then 0.41 g (1.06 mmol) of sodium borohydride was added in several portions, with stirring, over a period of 10 min. The solution began to become more homogeneous and lighter in color. After 15 min a yellow solid began to separate. After the mixture had been stirred for another 45 min, it was poured into 50 mL of water. The resulting mixture was extracted twice with chloroform and the combined extracts were washed with water and dried over anhydrous sodium sulfate. Removal of volatiles at reduced pressure left a yellow solid which was recrystallized from chloroform–hexane to give 0.29 g (88%) of (π,π'-benzhydrol)bis(tricarbonylchromium), yellow platelets, mp 147–149 °C. Anal. Calcd for $C_{19}H_{12}O_7Cr_2$: C, 50.01; H, 2.66. Found: C, 49.94; H, 2.66. NMR ($CHCl_3$): δ 2.58 (d, J = 5 Hz, 1 H, OH), 5.08 (d, J = 5 Hz, CH), and 5.20–5.84 ppm (m, 10 H, phenyl). IR ($CHCl_3$): ν(CO) 1950, 1896 cm^{-1}.

Similar reduction of (π,π'-3,3′-dimethylbenzophenone)bis(tricarbonylchromium) gave (π,π'-di-*m*-tolylcarbinol)bis(tricarbonylchromium), yellow plates, mp 147–149 °C, in 80% yield. Anal. Calcd for $C_{21}H_{16}O_7Cr_2$: C, 52.07; H, 3.33. Found: C, 51.76; H, 3.64. NMR ($CDCl_3$): δ 2.24, 2.25 (2 s, 6 H, CH_3), 2.74 (d, J = 4 Hz, 1 H, OH), and 5.00–5.67 ppm (m, 9 H, phenyl and CH). IR ($CHCl_3$): ν(CO) 1983, 1975, and 1910 cm^{-1}. ^{13}C NMR ($CDCl_3$, proton decoupled): δ_C 233.4 (terminal carbonyls); 18 resonances between δ_C 114.05 and 88.38 (phenyl ring carbons); 73.16, 73.06, and 72.85 (CH(OH)); and 21.38 ppm (CH_3).

For this compound one should see only six resonances for the phenyl ring carbon atoms and one resonance for the methinyl carbon atom.

The ^{1}H NMR spectrum also shows more than one resonance for the methyl protons and in the IR spectrum in the terminal carbonyl region the A_1 band is split into two bands. Thus all spectra are more complex than one might expect. There should be hindered rotation about the methinyl-to-ring carbon bonds, and, since the *m*-tolyl groups are not symmetrical, three stereoisomers will result, one of which will exist as a *dl* pair. These considerations are confirmed by inspection of molecular models, and thus the complexity of the spectra is explained.

Preparation of (π,π'-Di-*p*-tolylcarbinol)bis(tricarbonylchromium) by Direct Reaction. A 500-mL, three-necked, round-bottomed flask, equipped with a wide bore reflux condenser topped with a no-air stopper through which were placed a needle for a nitrogen inlet and a copper wire for scraping sublimed $Cr(CO)_6$ back into the flask, was flame dried, flushed with nitrogen, and charged with 9.00 g (41 mmol) of di-*p*-tolylcarbinol, 17.60 g (80 mmol) of chromium hexacarbonyl, 100 mL of diglyme (distilled from sodium benzophenone ketyl), and 200 mL of *n*-octane. The flask contents were shielded from light by a covering of aluminum foil. The mixture was heated under nitrogen at reflux for 18 h. Occasional scraping of the inside of the reflux condenser with the copper wire served to return sublimed chromium hexacarbonyl to the reaction mixture. After 18 h, the mixture was allowed to cool to room temperature and filtered. The residue was washed with acetone until the washings were colorless. The combined filtrate and washings were evaporated at reduced pressure and the yellow, oily residue was crystallized from chloroform/hexane. Recrystallization from this solvent pair gave 9.50 g (46%) of yellow prisms, mp 150–151 °C, of the title compound. Anal. Calcd for $C_{21}H_{16}O_7Cr_2$: C, 52.07; H, 3.33. Found: C, 51.99; H, 3.34. NMR ($CDCl_3$): δ 2.06 (s, 6 H, CH_3), 2.50 (d, J = 4 Hz, 1 H, OH), 4.94–5.94 ppm (m, 9 H, phenyl and CH). ^{13}C NMR ($CDCl_3$): see Table I. IR ($CHCl_3$): ν(CO) 1965, 1890 cm^{-1}.

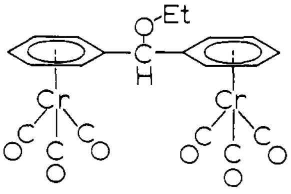
The title compound also was prepared in 47% yield by the reaction of 25 mmol of di-*p*-tolylcarbinol and 50 mmol of $(NH_3)_3Cr(CO)_3$ in 100 mL of *p*-dioxane for 4 h at reflux. Similar workup gave 5.70 g of product, mp 150–151 °C.

Preparation of the Carbonium Hexafluorophosphate Salts. The standard cation formation apparatus consisted of a 200-mL round-bottomed flask modified by the attachment of a straight 30-mm glass tuve with a coarse frit and a 19/38 standard taper male joint collinear with the neck of the flask. A 24/40 standard taper female joint was attached at an angle of 45° to the neck. The apparatus was equipped with a nitrogen inlet, no-air stopper, and magnetic stirring assembly, and a 100-mL, three-necked flask equipped with a nitrogen inlet and a glass stopper was attached to the 19/38 joint. When the apparatus contained solution, it was held horizontally and nitrogen was forced upward through the frit in order to prevent the solution from passing through the frit. During filtration, the apparatus was rotated to the vertical position and nitrogen pressure forced the solution through the frit into the attached three-necked flask.

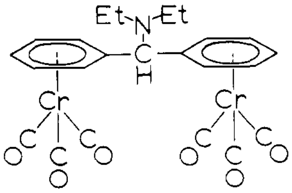
The standard cation formation apparatus was flushed with nitrogen, flame dried, and charged with the appropriate amount of (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium) in 50 mL of anhydrous benzene. A solution of 0.5 mL of 65% aqueous hexafluorophosphoric acid in 5 mL of propionic anhydride was prepared. After it had cooled to room temperature, it was added by syringe to the stirred solution of the alcohol. The yellow alcohol solution immediately turned blue and a blue solid precipitated. The mixture was filtered and the blue solid which had been collected on the frit was washed with three 50-mL portions of benzene and dried by passing nitrogen through it. The solid then was slurried in 25 mL of benzene and the appropriate nucleophilic substrate was added.

A sample of the blue (π,π'-di-*p*-tolylcarbonium hexafluorophosphate)bis(tricarbonylchromium) was dried in vacuo and submitted for analysis. Anal. Calcd for $C_{21}H_{15}O_6F_6PCr_2$: C, 41.19; H, 2.47. Found: C, 42.44; H, 2.87.

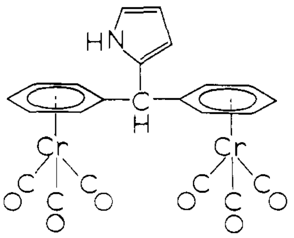
Reactions of (π,π'-Diphenylcarbonium hexafluorophosphate)bis(tricarbonylchromium) with Nucleophiles. A. With Ethanol. The standard cation exchange apparatus was flame dried, flushed with nitrogen, and charged with a slurry of 0.91 g (2.0 mmol) of (π,π'-benzhydrol)bis(tricarbonylchromium) in 3 mL of degassed propionic anhydride. A solution of 0.5 mL of 65% aqueous HPF_6 in 5 mL of degassed propionic anhydride was prepared and added to the slurry by syringe. The first drop caused the yellow slurry to become green and further addition gave a blue-green mixture. After the mixture had been stirred for 30 min, 20 mL of benzene was added. The mixture was filtered under nitrogen, leaving a royal blue solid which was washed with benzene and dried under a stream of nitrogen. Absolute ethanol (10 mL) then was added by syringe to the salt. The mixture became green, and after it had been stirred for 30 min, a yellow slurry was present. Addition of 30 mL of chloroform gave a yellow, homogeneous solution which was filtered, washed with water, and dried over anhydrous sodium sulfate. The solution was evaporated at reduced pressure and the residue was recrystallized from a chloroform/hexane mixture to give 0.52 g (54%) of (π,π'-benzhydryl ethyl ether)bis(tricarbonylchromium) (XXII), mp 142–144 °C dec. Anal. Calcd for $C_{21}H_{16}O_7Cr_2$: C, 52.07; H, 3.34. Found: C, 51.76; H, 3.38. NMR ($CDCl_3$): δ 1.40 (t, J = 6 Hz, 3 H, CH_3), 3.96 (q, J = 6 Hz, 2 H, CH_2), 4.62 (s, 1 H, CH), and 5.20–5.78 ppm (m, 10 H, Ph). IR ($CHCl_3$): ν(CO) 1971, 1900 cm^{-1}.


XXII

B. With Diethylamine. The blue hexafluorophosphate salt prepared as described above from 1.1 mmol of the alcohol was slurried in 10 mL of dry dichloromethane and 1 mL of diethylamine was added by syringe. An immediate reaction gave a yellow solution which was stirred for 15 min and filtered. The filtrate was washed with water, dried, and evaporated at reduced pressure. The oily solid which remained was filtered through a layer of Woelm alumina with chloroform. The chloroform solution was evaporated at reduced pressure and the residue was crystallized from chloroform/hexane to give 0.39 g (70%) of yellow crystals of (π,π'-benzhydryldiethylamine)bis(tricarbonylchromium) (XXIII), mp 133–135 °C. Anal. Calcd for $C_{23}H_{21}O_6NCr_2$: C, 54.01; H, 4.15; N, 2.74. Found: C, 53.80; H, 4.14; N, 2.62. NMR ($CDCl_3$): δ 1.35 (t, J = 7 Hz, 6 H, CH_3), 2.84 (q, J = 7 Hz, 4 H, CH_2), 4.74 (s, 1 H, CH), and 5.20–5.84 ppm (m, 10 H, Ph). IR ($CHCl_3$): ν(CO) 1979, 1972, 1901 cm^{-1}.


XXIII

C. With Pyrrole. A slurry of the carbonium ion salt prepared from 2.20 mmol of the alcohol was prepared in 25 mL of dry benzene and 1 mL of pyrrole was added by syringe. Workup as in B gave 0.80 g (72%) of yellow-brown crystals, mp 199–201 °C (from benzene/hexane), of (π,π'-2-benzhydrylpyrrole)bis(tricarbonylchromium) (XXIV).[33] Anal. Calcd for $C_{23}H_{15}O_6NCr_2$: C, 54.65; H, 2.99. Found: C, 54.41; H, 3.14. NMR ($CDCl_3$): δ 4.70 (s, 1 H, CH), 5.03–5.62 (m, 10 H, Ph), 5.95–6.22, 6.57–6.83, and 6.98–7.26 (m, 3 H, pyrrole), and 8.39 ppm (broad, 1 H, NH). IR ($CHCl_3$): ν(CO) 1950, 1900 cm^{-1}.


XXIV

Reactions of (π,π'-Di-*p*-tolylcarbonium hexafluorophosphate)bis(tricarbonylchromium) with Nucleophiles. (1) With Ethanol. The standard cation formation apparatus was flame dried, flushed with nitrogen, and charged with 1.00 g (2.0 mmol) of (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium). The carbonium ion salt was formed, washed, and dried as described in the general procedure. The blue hexafluorophosphate salt was in 25 mL of benzene and 10 mL of anhydrous ethanol was added by syringe, with stirring. The reaction mixture immediately became yellow and homogeneous. It then was poured into 50 mL of water and extracted with 100 mL of chloroform.

The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated at reduced pressure. The residual yellow oil was crystallized from chloroform/hexane to give 0.60 g (60%) of yellow platelets, mp 143–145 °C, of ether XVb. Anal. Calcd for $C_{23}H_{20}O_2Cr_2$: C, 53.90; H, 3.93. Found: C, 53.61; H, 3.85. NMR ($CDCl_3$): δ 1.32 (t, J = 7 Hz, 3 H, CH_3 of Et), 2.23 (s, 6 H, ring CH_3), 3.80 (q, J = 7 Hz, 2 H, CH_2), 4.47 (s, 1 H, CH) and 4.87–5.90 ppm (m, 8 H, Ph). IR ($CHCl_3$): ν(CO) 1965, 1892 cm^{-1}.

(2) **With Methanol.** The same procedure served in the reaction with methanol. The yellow reaction mixture was poured into water and extracted with benzene. The organic layer was washed with water, with 10% aqueous $NaHCO_3$, and again with water, with further workup as in (1) to give 0.78 g (75%) of yellow plates, mp 120–121 °C, of ether XVa. Anal. Calcd for $C_{22}H_{18}O_7Cr_2$: C, 53.02; H, 3.64. Found: C, 52.82; H, 3.68. NMR ($CDCl_3$): δ 2.21 (s, 6 H, ring CH_3), 3.62 (s, 3 H, OCH_3), 4.35 (s, 1 H, CH), and 4.83–5.90 (m, 8 H, Ph). IR ($CHCl_3$): ν(CO) 1968, 1900 cm^{-1}.

(3) **With Methylamine.** A slurry of the blue carbonium hexafluorophosphate in 25 mL of benzene was prepared from 2.00 mmol of the alcohol. In a separate 50-mL, three-necked flask, 20 mL of benzene was saturated with methylamine by passing a stream of the gaseous amine through the benzene for 2 min. This solution then was added by syringe to the carbonium ion salt slurry. Further processing as in (2) above gave an organic layer which was evaporated at reduced pressure to leave a yellow powder which was recrystallized from benzene to give 0.90 g (85%) of amine XVIa, mp 200 °C dec. Anal. Calcd for $C_{22}H_{19}O_6NCr_2$: C, 53.12; H, 3.85. Found: C, 53.55; H, 3.98. NMR ($CDCl_3$): δ 2.19 (s, 6 H, ring CH_3), 2.47 (s, 3 H, NCH_3), 3.80 (s, 1 H, CH), and 4.90–5.90 (m, 8 H, Ph).[34] IR ($CHCl_3$): ν(CO) 1964, 1890 cm^{-1}.

(4) **With *tert*-Butylamine.** A slurry of the carbonium ion hexafluorophosphate was prepared in 25 mL of benzene from 2.00 mmol of the alcohol and 5.0 mL (47 mmol) of *tert*-butylamine was added by syringe. The resulting yellow, homogeneous solution was processed as in B to give a yellow solid which was recrystallized from chloroform/hexane. The product amine, XVIc, was produced in 85% yield (0.90 g, mp 137–138 °C). Anal. Calcd for $C_{25}H_{25}O_6NCr_2$: C, 55.65; H, 4.67; N, 2.59. Found: C, 55.47; H, 4.57; N, 2.44. NMR ($CDCl_3$): δ 1.09 (s, 9 H, Me_3C), 2.22 (s, 6 H, ring CH_3), 4.08 (s, 1 H, CH), and 4.84–5.24 and 5.70–6.04 ppm (m, 8 H, Ph). IR (CCl_4): ν(CO) 1963, 1884 cm^{-1}.

(5) **With Isopropylamine.** A slurry of the carbonium ion hexafluorophosphate in 25 mL of benzene was prepared from 2.00 mmol of the alcohol and 1.0 mL (12 mmol) of isopropylamine was added by syringe. The resulting yellow, homogeneous solution was processed as in B, with the exception that dichloromethane was used instead of benzene to extract the reaction mixture after the water wash. One gram of yellow plates, mp 148–150 °C, was obtained by recrystallization from chloroform/hexane. These were found (analysis, NMR) to be the monochloroform solvate of the expected amine, XVIb. Anal. Calcd for $C_{24}H_{23}O_6NCr_2 \cdot CHCl_3$: C, 46.56; H, 3.75; N, 2.17. Found: C, 46.55; H, 3.75; N, 2.11. NMR ($CDCl_3$): δ 1.13 (d, J = 6 Hz, Me_2C), 2.18 (s, 6 H, ring CH_3), 2.90 septet, J = 6 Hz, Me_2CH), 4.03 (s, 1 H, CH), 4.87–6.13 (m, 8 H, Ph), and 7.21 (s, 1 H, $CHCl_3$). IR ($CHCl_3$): ν(CO) 1963, 1890 cm^{-1}.

The chloroform of solvation could not be removed by heating the complex under vacuum. An attempt was made to remove the chloroform by recrystallizing the complex from benzene. This only served to replace the molecule of chloroform with a molecule of benzene of solvation. The benzene adduct was characterized by elemental analysis and NMR spectroscopy. Anal. Calcd for $C_{24}H_{23}O_6NCr_2 \cdot C_6H_6$: C, 59.70; H, 4.84. Found: C, 59.49; H, 4.85. NMR ($CDCl_3$): δ 1.07 (d, J = 6 Hz, Me_2C), 2.11 (s, 6 H, ring CH_3), 2.83 (septet, J = 6 Hz, Me_2CH), 3.98 (s, 1 H, CH), 4.83–5.83 (m, 8 H, Ph), and 7.23 ppm (s, 6 H, C_6H_6). The benzene of crystallization could not be removed even by heating the complex at 100 °C at 0.03 Torr for 24 h.

(6) **With Diethylamine.** A slurry of the hexafluorophosphate in 25 mL of benzene was prepared from 2.00 mmol of the alcohol and 1.0 mL (11 mmol) of diethylamine was added by syringe. Further processing of the resulting yellow solution as in B gave a yellow solid. This was recrystallized from benzene/hexane to give 1.05 g (84%) of yellow plates, mp 161–162 °C, of amine XVId. Anal. Calcd for $C_{25}H_{25}O_6NCr_2$: C, 55.66; H, 4.67. Found: C, 55.44; H, 4.67. NMR ($CDCl_3$): δ 1.09 (t, J = 6 Hz, 6 H, $EtCH_3$), 2.19 (s, 6 H, ring CH_3), 2.64 (q, J = 6 Hz, 4 H, CH_2), 4.45 (s, 1 H, CH), and 4.91–5.80 ppm (m, 8 H, Ph). IR ($CHCl_3$): ν(CO) 1963, 1890 cm^{-1}.

(7) **With *N,N*-Dimethylaniline.** To a slurry of the carbonium ion salt in 25 mL of benzene, prepared from 1.5 mmol of the alcohol, was added 1.0 mL (7 mmol) of *N,N*-dimethylaniline. A yellow, homogeneous solution was formed immediately. The reaction mixture was poured into water and extracted with 50 mL of benzene. The organic layer was washed with 10% aqueous HCl, 10% aqueous $NaHCO_3$, and again with water. After it had been dried over $MgSO_4$ and filtered, the organic layer was evaporated at reduced pressure. The yellow solid which remained was recrystallized from chloroform/hexane to give 0.78 g (82%) of yellow plates, mp 209–211 °C, of amine XVII. Anal. Calcd for $C_{29}H_{25}O_6NCr_2$: C, 58.98; H, 4.27; N, 2.37. Found: C, 58.58; H, 4.22; N, 2.40. NMR ($CDCl_3$): δ 2.20 (s, 6 H, ring CH_3), 2.95 (s, 6 H, NCH_3), 4.55 (s, 1 H, CH), 4.80–5.63 (m, 8 H, benzhydryl Ph), and 6.50–7.23 ppm (AA′ BB′ m, 4 H, NC_6H_4). IR ($CHCl_3$): ν(CO) 1968, 1900 cm^{-1}.

(8) **With *N*-Methylpyrrole.** A slurry of the blue carbonium ion salt in 25 mL of benzene was prepared from 3.1 mmol of the alcohol and 1.0 mL (10 mmol) of *N*-methylpyrrole was added by syringe. The mixture became green and then yellow and homogeneous over a period of 10 min. It was stirred at room temperature for 15 min and then was processed further as in (2). The yellow solid which was obtained was recrystallized from methanol to give 1.18 g (69%) of yellow needles, mp 155–156 °C, which were identified as a 60:40 mixture of compounds XVIIIa and XVIIIb. Anal. Calcd for $C_{26}H_{21}O_6NCr_2$: C, 57.04; H, 3.87. Found: C, 56.89; H, 3.92. NMR ($CDCl_3$): δ 2.20 (s, 6 H, ring CH_3), 3.61 (s) and 3.71 (s) (3 H together, NCH_3), 4.49 (braod s, 1 H, CH), 4.81–5.59 (m, 8 H, Ph), and 5.59–6.70 ppm (m, 3 H, pyrrole H). The integrated ratio of the 3.77 and 3.61 ppm signals was 3:2, and this was taken to be the ratio of the 2- and 3-substituted products. IR ($CHCl_3$): ν(CO) 1962, 1890 cm^{-1}.

(9) **Attempted Reaction with *tert*-Butyl Alcohol and with Anisole.** A slurry of the carbonium ion salt in 25 mL of benzene which had been prepared from 2.0 mmol of the alcohol was treated with 1.0 mL (14 mmol) of *tert*-butyl alcohol. There was no apparent reaction. The blue slurry was stirred at room temperature for 5 h with no change in color. Water (5 mL) then was added. The mixture became yellow and homogeneous immediately. Further processing as in (1), using dichloromethane instead of chloroform to extract the organic phase, yielded 0.8 g (80%) of the starting alcohol XIV as the only product.

Anisole was similarly unreactive. After a 5-h period of attempted reaction between the carbonium hexafluorophosphate and anisole, water was added to the blue slurry. Further workup of the resulting yellow solution as above gave the starting alcohol in 85% recovery.

(10) **Chemistry of (π,π'-Benzhydrol)bis(tricarbonylchromium) in Trifluoroacetic Acid.** A sample of the alcohol complex was put into neat trifluoroacetic acid in order to generate the carbonium ion XIa for ^{13}C NMR study. A blue solution was formed, but after 15 min, some solid still was evident. The mixture was filtered and the dilute blue filtrate was filled into a ^{13}C NMR tube. After this solution had stood for 2 h, a yellow solid had formed and no ^{13}C NMR spectrum could be obtained. The yellow solid, mp 200 °C dec, was analyzed and identified as the ether XIX. Anal. Calcd for $C_{38}H_{22}O_{13}Cr_4$: C, 51.01; H, 2.48. Found: C, 50.69; H, 2.44. The IR spectrum (Nujol mull) showed a band at 1158 cm^{-1}, attributable to the C–O–C unit, as well as ν(CO) 1970, 1950, 1878 cm^{-1}.

^{13}C NMR Spectrum of the (π,π'-Di-*p*-tolylcarbonium chlorostannate)bis(tricarbonylchromium) Salt. A solution of 0.5 g of (π,π'-di-*p*-tolylcarbinol)bis(tricarbonylchromium) in 5 mL of degassed dichloromethane under nitrogen was cooled to −20 °C. To this stirred solution was added 0.5 mL (an excess) of tin tetrachloride. The solution immediately turned blue and some blue solid precipitated. However, enough material remained in solution to permit measurement of the ^{13}C NMR spectrum. The blue solution was filtered through a medium porosity frit into a 10-mm o.d. NMR tube equipped with a vortex plug. Hexafluorobenzene (0.3 mL) was added directly to the sample to serve as a lock sample. The tube was capped and maintained at −20 °C at all times. If this temperature was exceeded, decomposition invariably occurred.

The ^{13}C NMR spectrum was obtained using a modified Bruker HFX 90 spectrometer which was interfaced with a Digilab FTS/NMR-3 data system, and the signals reported are accurate to ±0.2 ppm. Using a pulse width of 10 μs (corresponding to a nutation angle of 30°), with a delay of 0.08 s, 10 000 pulses were required in order to obtain an adequate proton-decoupled spectrum. Off-resonance proton-decoupled spectra could not be obtained with the sample in a reasonable amount of time.

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(31) We draw carbonium ion XI with the $Cr(CO)_3$ groups in the transoid configuration, since, as molecular models show, this would minimize nonbonded repulsive interactions between CO ligands of the two $Cr(CO)_3$ groups. An x-ray diffraction study of the phenylbis(tricarbonylironcyclobutadiene)methyl cation (BF_4^- salt) established a transoid arrangement of the $Fe(CO)_3$ groups in that species,[16] and a transoid arrangement of $Cr(CO)_3$ groups was found in (π,π'-biphenyl)tricarbonylchromium, in which a planar organic ligand is present.[18]

(32) A general rule of thumb is that going from a neutral metal carbonyl to a cationic metal carbonyl, e.g., $Cr(CO)_6 \rightarrow Cr(CO)_6^+$, with a +1 charge raises ν(CO) by $\sim$100 cm^{-1}.[25]

(33) The assignment of the structure shown in XX is based solely on the known preferred site of reactivity of pyrrole in Friedel-Crafts acylations and alkylations.[29]

(34) The N-H resonances in this and the other two primary amine derived products were not observed. This is a general phenomenon in the ^{1}H NMR spectroscopy of primary and secondary amines since the N-H resonances are considerably broadened owing to the electric quadrupole moment of the ^{14}N nucleus: ref 30.

Control of Regioselectivity and Excited Singlet Reaction Rates by Substitution in the Di-π-methane Rearrangement. Mechanistic and Exploratory Photochemistry[1,2]

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Abstract: A series of 1,1,5,5-tetraaryl-3,3-dimethyl-1,4-pentadienes—with methoxy, cyano, and chloro substitution—was synthesized. The photochemistry of these compounds was investigated. Regioselectivity as a function of substitution was determined for the di-π-methane rearrangement. Reaction efficiencies were obtained. Also, single photon counting with deconvolution was employed to obtain the excited singlet rearrangement rates. The many facets of the rearrangement were investigated theoretically. SCF-CI calculations with multiple singly and doubly excited configurations were employed where necessary. A number of new concepts resulted. Our ΔP matrix treatment was used to determine the locus of excitation initially and during the reaction. Also, the experimental rate constants were found to parallel the calculated energies of bridging of the excited singlets to give the corresponding cyclopropyldicarbinyl diradicals. A hitherto unrecognized phenomenon of reaction inhibition by excessive vertical excited state stabilization was encountered. The electronic structure of the states of the cyclopropyldicarbinyl diradical was determined. Finally, control of the regioselectivity was considered from a theoretical standpoint.

Introduction

In our previous papers dealing with the divinyl version of the di-π-methane rearrangement[2,3] we observed an enhancement of the reaction efficiency and excited singlet rate constant on introduction of *p*-cyano groups. Conversely, we noted an efficiency and a rate inhibition arising from *p*-dimethylamino and *p*-methoxy substitution. Also unusual regioselectivity was encountered in which *p*-cyanophenyl groups appeared on the three-ring of product while *p*-methoxyphenyl and *p*-dimethylaminophenyl groups appeared preferentially on the

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