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The interaction of tricarbonyltoluenechromium with Lewis acids

Unlike bisarenechromium compounds, the arenetricarbonylchromium compounds readily undergo the standard electrophilic substitution reactions characteristic of an aromatic nucleus. The arene ring in the latter compounds, in this respect, resembles the cyclopentadienyl moiety in ferrocene. In contrast to bisarenechromium compounds and ferrocene and its derivatives, no stable cationic derivatives of arenetricarbonylchromium compounds have been reported, suggesting that the latter are more difficult to oxidize than are the bisarenechromium compounds. These observations and the reported oxidation potentials for dibenzenechromium[1] and ferrocene[2] suggest that the order of oxidative stability for these compounds is $ArCr(CO)_3 > (C_5H_5)_2Fe > Ar_2Cr$. Since both dibenzenechromium[3] and the metallocenes[4,5] react with strong π acids to form compounds which can be formulated as salts of radical anions, it was of interest to investigate the interaction of arenetricarbonylchromium compounds with π acids.

Experimental

Mixtures of tricarbonyltoluenechromium and Lewis acids were manipulated under an inert atmosphere using standard techniques in an attempt to isolate complex compounds from these systems and to show that some interaction occurs in solution.

Electron spin resonance spectra were determined with the equipment described previously[3].

Tricarbonyltoluenechromium was prepared by the method of Nicholls and Whiting[6], using the apparatus described by Strohmeier[7]. In a typical preparation, hexacarbonylchromium (6.0 g, 0.027 mole), toluene (8.67 g, 0.0942 mole), and 100 ml of diethylene glycol dimethyl ether ("diglyme") were heated at 180° for 5 h with stirring. The mixture was cooled, filtered, and the solvent and unreacted hexacarbonylchromium removed *in vacuo*. The residue was taken up in benzene, placed on an alumina column, and eluted with benzene; the eluent was concentrated and tricarbonyltoluenechromium precipitated as yellow crystals by the addition of light petroleum ether (3.07 g, 72 % based on hexacarbonylchromium consumed); m.p. 79.5–81.0° (Lit.[6] 82.5–83.5°).

The reaction of tricarbonyltoluenechromium with Lewis acids

Of the Lewis acids studied, 1,3,5-trinitrobenzene reactions with tricarbonyltoluenechromium to form the most stable product, and this system is described in detail. When mixtures of tricarbonyltoluenechromium and 1,3,5-trinitrobenzene in organic solvents are allowed to evaporate to dryness, slight decomposition occurs, but the main product is a red-brown crystalline substance. This product is soluble in a variety of solvents (*e.g.* acetone, benzene, dioxane, and tetrahydrofuran) to give yellow dilute solutions and red concentrated solutions.

An attempt was made to prepare a pure sample of this compound by mixing equivalent amounts of tricarbonyltoluenechromium and 1,3,5-trinitrobenzene in benzene. As the solvent was concentrated, the solution became progressively more red and began to deposit pale yellow crystals; only a few red crystals were formed. Ten volumes of light petroleum ether was then added to the residue and the solution evaporated; the orange-yellow crystals which formed first became progressively more red as the evaporation proceeded. The addition of petroleum ether to the residual slush caused the whole mass of crystals to turn red immediately. The crystals were isolated by filtration and dried without washing. (Found: Cr, 10.63. $C_{16}H_{11}CrN_3O_9$ calcd.: Cr, 11.79 %.)

Tricarbonyltoluenechromium can be removed from the red crystals by washing with light petroleum ether, leaving behind the sparingly soluble 1,3,5-trinitrobenzene (pale yellow).

The complex melted at 80–83° to a red liquid, $(C_6H_5CH_3)Cr(CO)_3$ melted at 76–78° to a yellow liquid, and the mixture melted at 67.5–69° to a red liquid. The infrared spectrum (KBr) of the red complex is essentially the sum of the spectra of the components. Ultraviolet spectral data for the red complex are summarized in Table 1.

All attempts to isolate complexes of tricarbonyltoluenechromium and the other Lewis acids yielded products which were obviously the result of decomposition. Highly colored solutions result when tricarbonyltoluenechromium is mixed with any one of a variety of Lewis acids (*e.g.*, maleic anhydride, *p*-benzoquinone, 1,3,5-trinitrobenzene, chloranil, and tetracyanoethylene) in dioxane, nitromethane and, where

TABLE 1

SPECTRAL DATA FOR THE $C_6H_3(NO_2)_3 \cdot (C_6H_5CH_3)Cr(CO)_3$ COMPLEX

Compound	$\lambda_{max.}$ *mμ (log ε)*
$(C_6H_5CH_3)Cr(CO)_3$	317 (3.94)[a]
$C_6H_3(NO_2)_3 \cdot (C_6H_5CH_3)Cr(CO)_3$ 2.59 × 10^{-5} *M* in C_6H_6	330 (~ 4.0)[a]
$C_6H_3(NO_2)_3 \cdot (C_6H_5CH_3)Cr(CO)_3$ 0.2 *M* in C_6H_6	335 (~ 3.2)[b]
$C_6H_3(NO_2)_3 \cdot (C_6H_5CH_3)Cr(CO)_3$ Nujol mull	315 (1.00)[c], ~ 480 (0.12)

[a] The presence of a maximum at or just below the lower wavelength limit of the spectrophotometer (200 mμ) is suggested by the shape of the absorption curve. [b] Appears as a band superimposed on a more intense band with a maximum < 300 mμ. [c] Relative intensities rather than log ε_{max} given.

solubility permitted, benzene. The colors which develop are different from those of either of the components. Dark colored viscous solutions or tarry solids were obtained when the solutions were evacuated.

Results and discussion

It is apparent that tricarbonyltoluenechromium interacts with Lewis acids when solutions of the components are mixed. The most stable of these complexes is that formed between 1,3,5-trinitrobenzene and the carbonyl with the formulation $(C_6H_5CH_3)Cr(CO)_3 \cdot C_6H_3(NO_2)_3$. The low chromium analysis is consistent with the observation that tricarbonyltoluenechromium can be leached from the complex with petroleum ether, suggesting that the complex is loosely bound.

Several methods of examining the nature of these complexes in solution were investigated. The results obtained from oscillometric titrations proved useless, even when 0.4 *M* solutions were used, and optical spectroscopic methods did not give unambiguous results. In the case of the red 1,3,5-trinitrobenzene complex the intense absorption band at 317 mμ associated with tricarbonyltoluenechromium overlaps with an absorption band of the complex (Table 1). Solutions containing tricarbonyltoluenechromium and trinitrobenzene exhibit a cut-off which rises more rapidly and begins at a lower energy (~ 285 mμ) than that of either of the components. The color of these solutions is concentration dependent, dilute solutions being yellow and concentrated solutions red, suggesting the presence of a system at equilibrium, the position of which in dilute solutions lies toward the components of the complex. Only one band (λ_{max} 330 mμ) is observed for dilute solutions but is difficult to use analytically since it overlaps with the band at 317 mμ associated with the carbonyl. The spectra of a dilute and a concentrated solution of a 1:1 molar mixture of the carbonyl and trinitrobenzene show the same features except that the band in the 330–335 mμ region at the latter concentration appears superimposed upon a much more intense general absorption. The spectrum of the solid compound (Nujol) also shows a broad lower intensity absorption centered at 480 mμ.

The green complexes formed between chloranil or tetracyanoethylene and tricarbonyltoluenechromium were investigated in solution using the continuous variations technique in an attempt to determine the stoichiometry for the interaction. Unfortunately these complexes appear to be photochemically unstable, successive scans of the same solution yielding different spectra.

Electron spin resonance measurements on solutions containing the carbonyl and the Lewis acids were more informative. In benzene, a solvent of low dielectric constant, ESR signals were not observed for mixtures of the carbonyl and any of the Lewis acids studied. However, radicals were detected in nitromethane solutions of the carbonyl and 1,3,5-trinitrobenzene, chloranil, or tetracyanoethylene. This phenomenon has been observed for complexes of amines with Lewis acids[8–10] and interpreted on the basis of competing equilibria (eqn. 1) which involve charge-transfer complexes (A·D) and electron-transfer complexes (A^-D^+). In media with low dielectric constants

$$\begin{tikzcd}
A + D \arrow[r, shift left] \arrow[d, shift left] & A\cdot D \arrow[l, shift left] \arrow[dl, shift left] & \\
A^-D^+ \arrow[u, shift left] \arrow[ur, shift left] \arrow[r] & \text{Secondary products} &
\end{tikzcd} \qquad (1)$$

the charge-transfer complex is favored, whereas electron-transfer occurs in high dielectric media. From previous work[3] it might be expected that complexation occurs through the chromium atom in tricarbonyltoluenechromium. The difficulties encountered in isolating complexes from media with high dielectric constants is a reflection of the fact that arenetricarbonylchromium compounds do not form stable cationic species; thus, the favored reaction in high dielectric media is the rapid formation of secondary products (eqn. 1). The isolation of a loosely bound complex of tricarbonyltoluenechromium with trinitrobenzene but not with the other Lewis acids studied, is consistent with the facts that trinitrobenzene is the weakest of these Lewis acids and that dibenzenechromium, which forms stable cationic species more readily than tricarbonyltoluenechromium, forms electron–transfer products with all the Lewis acids studied. The results reported here suggest that the charge-transfer complexes formed by tricarbonyltoluenechromium in media with low dielectric constants are loosely bound.

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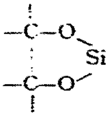
Cyclic esters of silicon containing a six-membered ring: (1,8-naphthalenedioxy)silanes*

Studies have been reported of five- and seven-membered heterocyclic systems containing silicon bonded through oxygen to aromatic rings[1,2]. It was found that the five-membered systems are in all cases less stable to hydrolysis and, while model studies show the  ring to be sterically feasible, upon standing the five-

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[*] The *Ring Index* recommendation for these systems is either naphtho[1,8-*de*]-2-sila-*m*-dioxin or naphtho[1,8-*de*]-1,3,2-dioxasiline. In conformity with our previous reports, we name these compounds as derivatives of silane in this communication.