The example cited is quite analogous to the reaction of $KMnO_4$ and IF_5 which yields $MnO_3F + IOF_3$.[15] The isolation of IOF_3 or compounds with an Sb–O bond from the perchlorate solvolysis reaction mixture would aid in elucidating the reaction mechanism.

The inability of BF_3 to promote the solvolysis of perchlorate in an HF medium confirms that BF_3 is not a strong acid in HF.[16] Acid strengths in HF decrease in the order $SbF_5 > PF_5 > BF_3$,[5,16] which is consistent with the slightly higher yields and lower reaction temperature observed for SbF_5 in comparison with AsF_5 (Table I).

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Kinetic and Synthetic Studies of Olefin and Acetylene Complexes of Hexamethylbenzenetricarbonylchromium

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Recent kinetic studies indicate that the reactions of $C_5H_5Mn(CO)_2(olefin)$ with phosphines, L, to form $C_5H_5Mn(CO)_2(L)$ proceed by way of an S_N1 mechanism.[1] The rates of reaction vary greatly with the nature of the olefin. In an attempt to understand the behavior of olefins in similar compounds, we prepared several complexes of the type $(H_3C)_6C_6Cr(CO)_2(olefin)$. Since it had previously been reported[2] that some of these complexes reacted with $P(C_6H_5)_3$ to form $(H_3C)_6C_6Cr(CO)_2P(C_6H_5)_3$, we planned to examine the kinetics of these reactions. For reasons of instability, insolubility, or unreactivity, however, it was possible to study extensively only the reaction of $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$ with several nucleophiles

$$(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5) + L \xrightarrow{C_6H_6} (H_3C)_6C_6Cr(CO)_2(L) + C_6H_5C{\equiv}CC_6H_5 \quad (1)$$

In this paper, we report the synthesis of several $(H_3C)_6C_6Cr(CO)_2(olefin)$ derivatives and the results of the kinetic study of reaction 1.

Experimental Section

Preparation and Purification of Materials.—$(H_3C)_6C_6Cr(CO)_3$[3] and $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$[2] were prepared using procedures reported in the literature. Reagent grade $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ were not purified further. The $P(n\text{-}C_4H_9)_3$ was purified by fractional distillation at reduced pressure. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ immediately before use. Reagent grade benzene was saturated with N_2 before using.

The $(H_3C)_6C_6Cr(CO)_2(olefin)$ complexes were prepared by irradiating in a quartz tube a solution, under a nitrogen atmosphere, of 40 ml of THF containing 0.005 mol of $(H_3C)_6C_6Cr(CO)_3$ and a slight excess of the desired olefin for 4–5 hr with a Hanovia ultraviolet lamp. Details of isolation and characterization of the complexes from the irradiated solutions are given below.

$(H_3C)_6C_6Cr(CO)_2$(maleic acid).—The red THF solution was concentrated to 20 ml under a water-aspirator vacuum. After filtration, the resulting crystals were washed with benzene to remove unreacted $(H_3C)_6C_6Cr(CO)_3$ and then with CH_3OH to remove excess maleic acid. The yield of the red-orange crystals was 0.96 g (49%).

Anal. Calcd for $(H_3C)_6C_6Cr(CO)_2(C_4H_4O_4)$: C, 55.95; H, 5.75. Found: C, 55.85; H, 5.81. The compound decomposes at 143–145° and is stable in air for several weeks.

$(H_3C)_6C_6Cr(CO)_2$(fumaric acid).—This compound was isolated in the same manner as for the maleic acid complex. Owing to the instability of the complex, all operations must be carried out in a nitrogen atmosphere. The yield was 43%.

Anal. Calcd for $(H_3C)_6C_6Cr(CO)_2(C_4H_4O_4)$: C, 55.95; H, 5.75. Found: C, 55.65; H, 5.76. The complex decomposes at 133–135°, and its solutions decompose rapidly in air.

$(H_3C)_6C_6Cr(CO)_2$(endic anhydride).—The irradiated solution was filtered and evaporated to dryness under vacuum. The resulting yellow-orange crystals were dissolved in 25 ml of benzene, leaving unreacted endic anhydride (*endo-cis*-bicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic anhydride). After filtration, the solution was evaporated to 15 ml, and the product (73% yield) precipitated upon adding 25 ml of heptane.

Anal. Calcd for $(H_3C)_6C_6Cr(CO)_2(C_9H_8O_3)$: C, 63.58; H, 6.03. Found: C, 61.45; H, 5.98. The compound decomposes at 123–125° and in air slowly at room temperature.

Other complexes—$(H_3C)_6C_6Cr(CO)_2$(maleic anhydride), $(H_3C)_6C_6Cr(CO)_2$(citraconic anhydride), and $(H_3C)_6C_6Cr(CO)_2(H_3CO_2CC{\equiv}CCO_2CH_3)$—were prepared similarly and identified only by their characteristic infrared spectra (Table I).

TABLE I
C–O STRETCHING FREQUENCIES OF $(H_3C)_6C_6Cr(CO)_2(olefin)$

Olefin	Solvent	C–O str, cm^{-1}	
Cyclopentene	Benzene	1883	1835[a]
Endic anhydride	Benzene	1902	1838
$C_6H_5{\equiv}CC_6H_5$	Benzene	1912	1835[a]
Fumaric acid	KBr	1933	1861
Maleic acid	KBr	1924	1870
Citraconic anhydride	$CHCl_3$	1959	1893
Maleic anhydride	$CHCl_3$	1967	1906

[a] Reference 2.

Determination of Rates of Reaction.—Freshly prepared benzene solutions of $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$, $\sim 1 \times 10^{-3}$ *M*, and of the ligand L were placed separately under N_2 in a two-leg reaction flask fitted with a serum cap. Since laboratory light causes considerable decomposition of the complex, the reaction vessel was carefully wrapped with aluminum foil. After thermostating the vessel at the desired temperature (±0.05°) for about 15 min, the reaction was started by tilting and mixing the solutions in the two legs of the vessel. At appropriate time intervals, a sample was withdrawn with a syringe and the absorbance of the solution at 500 mμ was determined on a Cary 14 ultraviolet–visible spectrophotometer. At this wavelength the reactant absorbs quite strongly whereas the extinction coefficients for the products, $(H_3C)_6C_6Cr(CO)_2(L)$, are

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[1] R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967).

[2] W. Strohmeier and H. Hellmann, *Chem. Ber.*, **98**, 1598 (1965).

[3] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

low. The pseudo-first-order rate constants, k_{obsd}, were obtained from slopes of plots of ln $(A - A_\infty)$ *vs.* time. Such plots were linear to at least 70% completion of the reaction.

In the absence of ligand, $(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$ decomposed at a rate which was approximately 45% of that of the substitution reaction. This decomposition was accompanied by the formation of a green precipitate. In the presence of ligand, however, no precipitate formed and both the ultraviolet–visible and the infrared spectra indicated that $(H_3C)_6C_6Cr(CO)_2(L)$ was the only product.

From the values of k_{obsd} at six different temperatures (Table III) were calculated the enthalpy and entropy of activation together with their standard deviations.[4]

Results and Discussion

Infrared Spectra of $(H_3C)_6C_6Cr(CO)_2$(olefin) Complexes.—The C–O stretching frequencies of these complexes are given in Table I. The frequencies significantly increase with the nature of the olefin: hydrocarbon olefin < acid-bearing olefin < anhydride-bearing olefin. This trend suggests an increase in Cr to olefin π bonding in the same order. The stability of these complexes toward decomposition in air also follows the same order. That π bonding from Cr to the olefin is of importance is supported by the decrease in the >C=O stretching frequencies of the anhydride group upon coordination to the metal. For example, these absorptions of maleic anhydride (1850 and 1777 cm^{-1}) shift to 1810 and 1743 cm^{-1} in $(H_3C)_6C_6Cr(CO)_2$(maleic anhydride). The same is true for citraconic anhydride whose >C=O bands shift from 1830 and 1760 to 1803 and 1734 cm^{-1} upon complexation. The weakening of these >C=O bonds is consistent with significant π bonding from the Cr into the olefin π system. Endic anhydride behaves, as expected, like a simple hydrocarbon olefin since the anhydride group is removed from the olefinic bond by a saturated carbon atom.

It should be mentioned that all of these metal–carbonyl stretching frequencies are higher than those of analogous complexes with amine or phosphine donors. The C–O absorptions of $(H_3C)_6C_6Cr(CO)_2P(C_6H_5)_3$, for example, occur at 1873 and 1810 cm^{-1}.[5]

Kinetics of Reaction 1.—The k_{obsd} values given in Table II clearly indicate that the rate of reaction 1 is independent of the nature and concentration of L and obeys the rate law

$$\text{rate} = k[(H_3C)_6C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)]$$

Such a rate law suggests an SN1 mechanism in which the rate of $C_6H_5C{\equiv}CC_6H_5$ dissociation is rate determining. The positive value of the entropy of activation (+12.5 eu) supports this mechanism (Table III). The enthalpy of activation (27.9 kcal/mol) is somewhat lower than obtained for olefin dissociation from most of the $C_5H_5Mn(CO)_2$(olefin) complexes.[1]

Attempts to study the analogous reaction of 1,3,5-$(H_3C)_3H_3C_6Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$ were frustrated by the instability of solutions of the complex. At the other extreme, $(H_3C)_6C_6Cr(CO)_2$(maleic anhydride) and $(H_3C)_6C_6Cr(CO)_2$(citraconic anhydride) do not react with $P(C_6H_5)_3$ or $P(n\text{-}C_4H_9)_3$ even in boiling benzene.

TABLE II

RATE OF REACTION 1 IN BENZENE AT 40.0°

L	[L], *M*	10^4k_{obsd}, sec^{-1}
$P(C_6H_5)$	0.005	1.20
	0.010	1.19
	0.020	1.11
	0.025	1.12
	0.040	1.22
	0.050	1.06
$As(C_6H_5)_3$	0.005	1.06
	0.025	1.20
	0.050	1.23
$P(n\text{-}C_4H_9)_3$	0.005	1.14
	0.025	1.22
	0.050	1.17
$P(OC_6H_5)_3$	0.005	1.42
	0.050	1.19

TABLE III

RATE CONSTANTS FOR REACTION 1[a] IN BENZENE

Temp, °C	10^4k, sec^{-1}
40.0	1.15
45.0	2.37
50.0	4.78
52.5	6.72
55.0	9.41
60.0	18.2

[a] $\Delta H^* = 27.9 \pm 0.7$ kcal/mol; $\Delta S^* = 12.5 \pm 2.0$ eu. Limits of error are one standard deviation.

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Coordination Complexes of Niobium and Tantalum. VI. Seven-Coordinated Oxalatoniobates(V) and -tantalates(V)[1]

BY NEVENKA BRNIČEVIĆ AND CIRILA DJORDJEVIĆ[2]

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Oxalato derivatives of niobium and tantalum have been investigated only a few times previously.[3] These species are of interest, since they represent one of the few types of complexes of these metals which are stable in aqueous solution and because oxalic acid is one of the most common agents for dissolving niobium and tantalum pentoxides. The chemistry of these solutions, however, is vague and confused. It is obvious that several complex oxalatometal species exist in solution. Their presence and concentration are

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[1] Part V: C. Djordjević and N. Vuletić, *Inorg. Chem.*, **7**, 1864 (1968).

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