apparent in the patterns may indicate structural similarities. Single crystal studies are now in progress on BiS_2 elsewhere,[4] and studies of the structures of the related compounds are planned.

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[4] Robert A. Jacobson, to be published.

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The Reduction of Potentiometric Hydrolysis Data[1]

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Potentiometric measurement of acidity is perhaps the most widely used method of investigating cation hydrolysis in aqueous solutions. Such measurements, usually employing the glass electrode, have become quite precise ($< \pm 0.1$ mv. or $< \pm 0.002$ pH unit) owing to the sensitive electrometers now in use. Variations in ionic activity coefficients are reduced to low values[2a] by maintenance of a relatively high and constant ionic strength compared with the changes in the concentration of acid and in the concentration of the metal ion being studied. Provided the salt bridge or the reference electrode used contains a solution similar in composition to the solutions being measured, the effect of liquid junction potentials, while appreciable, can be estimated with sufficient accuracy.[2b] Often the largest errors which can appear in such studies are introduced by unsuspected errors in the compositions of the solutions used or by the manner in which the experimental data are reduced to yield the amount of hydrolysis as a function of acidity and metal ion concentration.

It is the purpose of this note to describe briefly the method of hydrolysis data reduction which we have developed in the attempt to do justice to the precision which now appears attainable in such potentiometric measurements. This method was usually used to treat data from runs (titrations) well on the acid side of neutrality, as is usually true in the study of cation hydrolysis, and hence the concentration of OH^- could be neglected in the hydrolyzing solution. With obvious modifications, the same general procedure can be used in dealing with pH data from more basic media (*cf.* footnote *d*, Table I) or with potentiometric data wherein the concentration of some ion other than H^+ is being measured.

The conversion of the data for each point in a potentiometric titration to a value of the hydroxyl number ($\bar{n}$), the average number of OH^- ions per hydrolyzing metal ion M^{z+} in solution, and the corresponding acid concentration is simple in principle but involved and laborious in practice. The basic steps used (*cf.* Table I) are: (1) to compute, from the volumes and compositions of the initial cell solution and titrant solution, the acidity (m_H) which is expected in the absence of hydrolysis, (2) to compute from the measured e.m.f. the actual acidity (h), and (3) to compute from these two quantities and the concentration of the hydrolyzing cation the hydroxyl number ($\bar{n}$).

To obtain $\bar{n}$ and h values, it is desirable in addition to compute the concentrations of all ionic species in the solution since they affect the liquid junction potential which can in turn appreciably affect the measured e.m.f. values. The inclusion of liquid junction terms in the equation relating the cell e.m.f. to the acidity requires an iterative solution for the acidity (h). Finally, the completed computation often shows that systematic errors are present which significantly affect $\bar{n}$ in the important initial stages of hydrolysis; in this region the differences $h - m_H$ on which $\bar{n}$ depends are small and quite sensitive functions of the assigned values of the initial acidity ($m_{H,0}$), the reference acidity (h_r), and a liquid junction parameter (D_H). This necessitates corrections of these quantities and a recalculation of the data. In our hydrolysis studies, data reduction has, to an increasing extent, been performed with the aid of the 7090 computer.[3]

As the equation in Table I (2) indicates, the *changes* in observed cell potential are related to the *changes* in acidity and the *changes* in liquid junction potential which occur during a titration. The reference point, at which $\Delta E = 0$, is usually the point in the titration, at the beginning or the end, at which the acidity is highest. If hydrolysis of the cation being studied is negligible here, h_r may be taken as equal to m_H, otherwise h_r is determined indirectly (*vide infra*). The form in which the liquid junction potential is represented was derived from the Henderson equation[2c] when applied to titrations in which the ionic strength is held constant and the concentrations that vary are low compared with the inert electrolyte concentration. The coefficients, D_i, can be estimated from the equivalent conductance, λ_i, and charge (with sign), Z_i, of each ion

$$D_i = RT\lambda_i/(Z_iF\Sigma\, m_i\lambda_i) \qquad (1)$$

or they can be measured experimentally in titrations not involving hydrolysis. Strictly, the last term in the equation for ΔE should be of the form $\Sigma D_i(i_r - i)$, in which the actual concentration of each ion other than H^+ appears. Such usage would require a fore-knowledge of the hydrolysis reactions being investigated.

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962): (a) footnote 16, p. 786; (b) Table I; (c) footnote 12, p. 783.

[3] The computer programs employed were written by R. J. McNamee of the Operations Analysis Division, Oak Ridge Gaseous Diffusion Plant.

Table I

Reduction of Hydrolysis Data

Quantities Specified for Each Titration[a]	
$m_{i,0}$, V_0, d_0, g_0	Values for initial cell solution
$m_{i,t}$, d_t, g_t	Values for titrant solution
h_r, $m_{i,r}$	Values for solution chosen as reference point of titration
D_i	Liquid junction parameters for each ion
Quantities Specified for Each Point in Titration	
V_t	The total volume of titrant solution added
ΔE	The difference between observed e.m.f. and the e.m.f. at reference point of titration
Computations for Each Point in Titration	
(1) m_i	The molality of each ion, from $m_i = m_{i,0} + W(m_{i,t} - m_{i,0})$ where W is the dilution factor[b] $V_td_tg_t/(V_0d_0g_0 + V_td_tg_t)$
(2) h	The acid concentration, by iterative solution of the equation $\Delta E = \underbrace{\frac{RT}{F}\ln(h_r/h)}_{\text{(Nernst term)}} - \underbrace{D_H(h_r - h)}_{\text{(L.J.P.}^c\text{ term for H}^+)} - \underbrace{\Sigma D_i(m_{i,r} - m_i)}_{\text{(L.J.P.}^c\text{ terms for other ions)}}$
(3) $\bar{n}$	The hydroxl number, from[d] $\bar{n} = (h - m_H)/m_M$

[a] m_i = formal molality of each ion, i = true molality of each ion (*e.g.*, m_H and m_M are formal acidity and formal molality of hydrolyzable cation, h is the true acidity), V, d, g = volume, density, and grams of water per gram of solution. [b] If molarities are used instead of molalities and if the volume change on mixing may be neglected, the product dg is replaced by unity and $W = V_t/(V_0 + V_t)$. [c] Liquid junction potential. [d] In the notation used m_H is negative for formally basic solutions; *i.e.*, $m_H = -m_{OH}$. The complete expression for $\bar{n}$ is $([h] - [OH^-] - m_H)/m_M$. The simpler expression shown in part (3) is valid in the acid region where $[H^+] >> [OH^-]$. In the neutral region $\bar{n} = (h - (Q_W/h) - m_H)/m_M$, wherein Q_W is the equilibrium quotient for the self-dissociation of water; in the basic range, $\bar{n} = (m_{OH} - [OH])/m_M$.

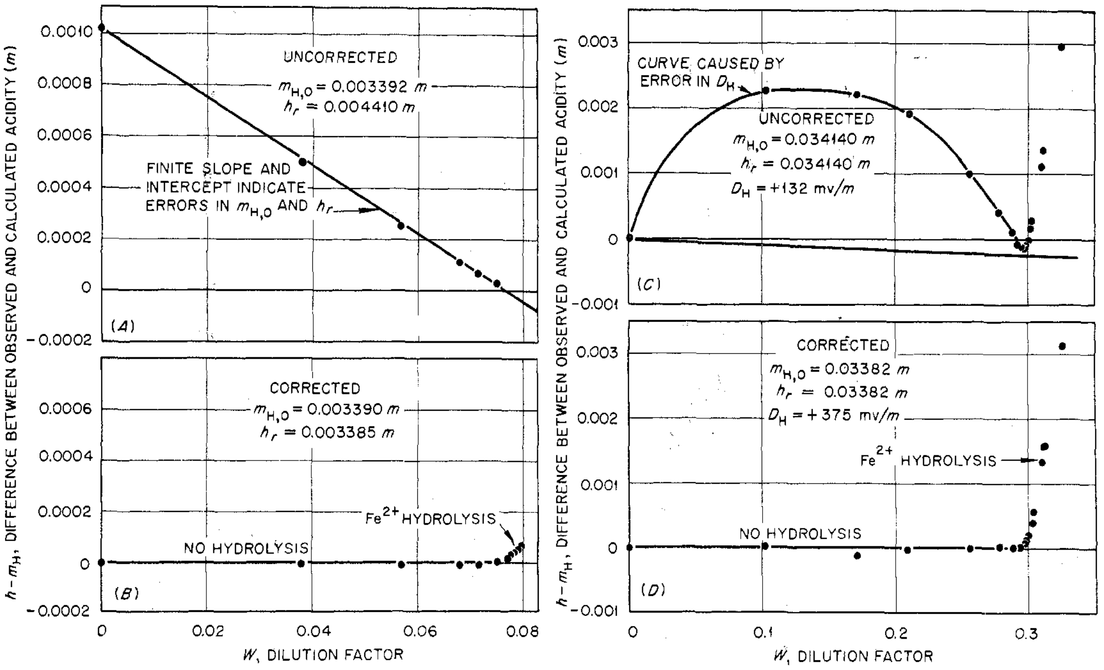

Figure 1.—Deviation of the calculated acidity from the formal acidity in titrations of $FeCl_2$–HCl–0.1 m (Na)Cl solutions at 95°. The dilution factor, W, is proportional to the amount of added base. (A) and (B) illustrate the effect and correction of a large error in h_r; (C) and (D) illustrate the effect and correction of a large error in D_H.

Usually, however, the influence of the changing concentrations of the hydrolyzing ion and its hydrolysis products on the liquid junction potential may be adequately represented by $D_M(m_{M,r} - m_M)$; recalculation of the data with inclusion of all the liquid junction terms prescribed by the indicated hydrolysis mechanism showed such effects to be negligible in studies of UO_2^{2+} [2] and Th^{4+} [4] hydrolysis.

The computed results of an acid–base titration are inspected by plotting $h - m_H$ (the difference between the measured acidity and that expected for no hydrolysis) *vs.* W (the dilution factor), which is approximately proportional to the amount of titrant added and is a linear function of the formal acidity (*cf.* Table I (1)). Ideally, if hydrolysis was negligible at the point of highest acidity, then from this point in the titration (at either the beginning or the end) the data on such a plot should lie on a line of zero slope and zero intercept which is terminated by an upward break at the point in the titration where hydrolysis first becomes detectable (Figure 1). If, however, an error has been made in $m_{H,0}$ and/or h_r, the data in this region define a line of finite slope and intercept indicating significant (and erroneous) values of $\bar{n}$. The slope (S) and intercept (I) of this line can be used to correct $m_{H,0}$ and h_r as follows[5]

$$m_{H,0}^c = (m_{H,0} + I)(m_{H,t}^c)/(m_{H,t} + S + I) \qquad (2)$$

$$h_r^c = h_r(m_{H,t}^c)/(m_{H,t} + S + I) \qquad (3)$$

wherein the superscript c denotes the corrected values. It is usually assumed that $m_{H,t}^c = m_{H,t}$, since the composition of the titrant usually is the most accurately known quantity. Further, it can be shown that if an error has been made in D_H (which determines the value of the largest liquid junction potential term), the otherwise linear curve will be approximately parabolic. If the highest acidity is taken as h_r, the correction in D_H required to reduce this curve to a straight line is given by the approximation[6a]

$$D_H^c \sim D_H + \frac{4RT}{F}\frac{\Delta(h - m_H)}{h_r^2} \qquad (4)$$

wherein, $\Delta(h - m_H)$ is the deviation of the parabola from the expected straight line at the point where $m_H = {}^1/_2 h_r$. The use of these correction procedures is illustrated by the somewhat exaggerated examples in Figure 1.

These correction procedures have been very useful as a means of eliminating small errors in $m_{H,0}$, h_r, and D_H and, at the same time, of verifying the validity of the equation in Table I (3) in systems where hydrolysis is unappreciable at acidities $>\sim 0.01\ m$.

If hydrolysis is appreciable at the highest acidity which can be measured accurately—and hence h_r can at no point be placed equal to m_H—it is necessary to perform titrations in which the initial cell solution contains only acid in order to establish h_r. The titrant contains the hydrolyzing cation and m_H is the primary quantity varied. The computed results of such titrations—$\bar{n}$ as a function of m_M and h—may be used to fix h_r in other, acid–base, titrations in which acidity is the primary quantity varied.

Often the principal uncertainty in this latter procedure arises from the error in estimating D_M. To a good approximation[6b]

$$\bar{n}^c \sim \bar{n} + \frac{(D_M^c - D_M)h}{RT/F} \qquad (5)$$

In all measurements, errors introduced into $\bar{n}$ by errors in h are given by

$$\bar{n}^c - \bar{n} + (h^c - h)/m_M \qquad (6)$$

Hence, when the acidity is increased or the concentration of the metal ion being studied is decreased, the accuracy with which $\bar{n}$ can be measured is decreased.

Comparison of observed values of D_i with values calculated from limiting equivalent conductances (eq. 1) suggests the uncertainty in D_M is less than ±10 mv./kg. mole^{-1} for ionic strengths in the range 0.5–1 m. From eq. 5 the corresponding uncertainties in $\bar{n}$ at 25° would be $< \pm 0.004$ for $h \leq 0.01$. If h has an uncertainty of ±0.5% (±0.12 mv. in ΔE at 25°), then from eq. 6 the corresponding uncertainty in $\bar{n}$ would be <0.005 with $h \leq m_M$. Within these limits ($h < 0.01\ m$ and $< m_M$), the accuracy with which $\bar{n}$ may be determined is more often limited by errors in solution composition and protolytic impurities than by errors in the e.m.f. measurements or in liquid junction potential corrections.

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[4] C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts *Inorg. Chem.*, **4**, 518 (1965).

[5] If hydrolysis is negligible then from the equation in Table I (1), $h^c = m_{H,0}^c + W(m_{H,t}^c - m_{H,0}^c)$. If h_r is erroneous, the resulting erroneous value of h is given by $h = (h_r/h_r^c)h^c$ if the error is small. Similarly, if $m_{H,0}$ and $m_{H,t}$ are erroneous, the resulting erroneous value of m_H is given by $m_H = m_{H,0} + W(m_{H,t} - m_{H,0})$. These equations may be combined to give the linear relationship $h - m_H = I + SW$, wherein $I = (h_r/h_r^c)m_{H,0}^c - m_{H,0}$; $S = (h_r/h_r^c)(m_{H,t}^c - m_{H,0}^c) - (m_{H,t} - m_{H,0})$. These expressions for I and S may be solved for the corrected values h_r^c and $m_{H,0}^c$, giving eq. 2 and 3.

[6] (a) The effect of an erroneous value of D_H may be deduced from the equation in Table I (2). Denoting the correct values by superscript c

$$\frac{RT}{F}\ln(h_r/h^c) - D_H^c(h_r - h^c) = \frac{RT}{F}\ln(h_r/h) - D_H(h_r - h)$$

This may be simplified to

$$\frac{RT}{F}\ln(h/h^c) = D_H^c(h_r - h^c) - D_H(h_r - h)$$

If the error is small, ln (h/h^c) may be replaced by $(h/h^c) - 1$ and the resulting expression rearranged to

$$h - h^c = \frac{(D_H^c - D_H)(h_r - h^c)h^c}{(RT/F) - D_Hh^c} \sim \frac{(D_H^c - D_H)(h_r - h^c)h^c}{RT/F}$$

(since RT/F is usually much larger than D_Hh^c). This last expression shows that the error in h resulting from an error in D_H varies approximately as the product $(h_r - h^c)h^c$, being zero at the point where $h_r = h^c$, and approaching zero as $h^c \rightarrow 0$. If the maximum acidity $= h_r$, then at the point of half-neutralization—with negligible hydrolysis—$h - h^c$ may be replaced by $\Delta(h - m_H)$, and $(h_r = h^c)h^c$ by $(h_1/2)^2$. These substitutions yield eq. 4. (b) The effect of an error in D_M is seen from

$$\frac{RT}{F}\ln(h_r/h^c) - D_H(h_r - h^c) - D_M^c(m_{M,r}^c - m_M) =$$

$$\frac{RT}{F}\ln(h_r/h) - D_H(h_r - h) - D_M(m_{M,r} - m_M)$$

For small errors this may be rearranged to

$$h - h^c = \frac{(D_M^c - D_M)(m_{M,r} - m_M)h^c}{(RT/F) + D_Hh^c} \sim \frac{(D_M^c - D_M)(m_{M,r} - m_M)h^c}{(RT/F)}$$

With $m_{M,r} = 0$, this simplifies to eq. 5.

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Hexafluoroacetylacetonato Derivative of Manganese Carbonyl[1]

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The reaction of metal carbonyls with 1,3-diketones was initially studied by Hieber,[2] who reported the formation of tris(acetylacetonato)iron(III) from iron pentacarbonyl and 2,4-pentanedione. Using the iron tetracarbonyl halides, Hieber and Bader[3] were able also to prepare the complexes formulated as $FeBr_2\cdot 2acac$[4] and $2FeCl_2\cdot 3acac$. More recently, Dunne and Cotton[5] prepared, in good yields, the compounds Mo(acac)$_3$, Mo(tfac)$_3$,[4] Cr(acac)$_3$, and Cr(tfac)$_3$ by refluxing the hexacarbonyls with 2,4-pentanedione and 1,1,1-trifluoropentane-2,4-dione. The chelate Mo(acac)$_3$ was also obtained from essentially the same reaction by Larson and Moore.[6] Later, Goan, *et al.*,[7] discovered that the conditions of this reaction and that of various diketones with the carbonyls of iron and chromium could be moderated when the mixtures are irradiated with ultraviolet light.

Thus, the above reactions of the metal carbonyls and their derivatives proceed to the simple chelates, and no intermediate mixed carbonyl acetylacetonates had been obtained despite some efforts of synthesis.[7]

Consideration of relative stabilities of low-valent transition metal complexes with hydrogen- and fluorine-containing ligands[8] prompted us to explore possible syntheses of such acetylacetonato compounds using highly fluorinated pentanediones. Described here is the first successful preparation of a 1,3-diketone derivative of manganese carbonyl, Mn(CO)$_4$(hfac).[4] Almost concurrently with the submission of this paper for publication, Bonati and Wilkinson[9] reported the synthesis of several rhodium(I) pentanedionato carbonyl complexes from rhodium(I) carbonyl chloride and β-diketones.

Experimental

Dimanganese decacarbonyl was purchased from the Ethyl Corporation. Hexafluoroacetylacetone, obtained from Columbia Organic Chemicals Co., was distilled before use. All solvents were dried over P_4O_{10} and fractionally distilled.

The proton magnetic resonance spectrum of the complex in CDCl$_3$ solution was recorded on a Varian A 60 instrument using tetramethylsilane as an internal reference. The molar conductivity of a nitromethane solution of Mn(CO)$_4$(hfac) was measured with a Model RC 16B2 conductivity bridge (Industrial Instruments, Inc.). The molecular weight ($1.7–1.8 \times 10^{-2}$ M solution in CHCl$_3$) was determined using a Mechrolab osmometer. Analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Mn(CO)$_4$(hfac).—In a typical preparation, chloropentacarbonylmanganese(I) (2.70 g., 12 mmoles), synthesized by the method of Abel and Wilkinson,[10] was dissolved in acetonitrile (250 ml.) to produce a clear pale yellow solution. Hexafluoroacetylacetone (2.55 g., 12 mmoles), also in acetonitrile (10 ml.), was added and the stirred mixture kept at 25° under a nitrogen atmosphere. Slow evolution of gas occurred over about 6 hr., during which time the color of the solution changed to dark amber. After allowing a total reaction time of 12 hr., the solution was evaporated to dryness (25°, $\sim$20 mm.). The resulting bright yellow solid was extracted with 30–60° petroleum ether (six 100-ml. portions), and the combined extracts were evaporated (25°, $\sim$20 mm.). The solid was then washed with two 2-ml. portions of petroleum ether and sublimed (55°, 0.01 mm.). The yield of the bright yellow Mn(CO)$_4$(hfac) (m.p. 99–100° dec.) was 0.63 g. (14%).

Anal. Calcd. for $C_9HO_6F_6Mn$: C, 28.9; H, 0.3; F, 30.5; Mn, 14.7; mol. wt., 374. Found: C, 28.9; H, 1.0[11]; F, 30.1; Mn, 14.8; mol. wt., 367, 365. The n.m.r. spectrum showed a single proton signal at τ 3.84.

The residue from the initial petroleum ether extractions of the product has not yet been fully characterized, although analyses indicate the empirical formula $C_9H_9O_6N_2Cl_2Mn_2$. Preliminary studies show this metal carbonyl derivative to have very low solubility in the majority of organic solvents, to be nonvolatile, and to decompose (80°, 0.01 mm.) to yield $Mn_2(CO)_{10}$.

The reaction of Mn(CO)$_5$Cl with hexafluoroacetylacetone was also carried out in acetonitrile using excess quantities of the diketone (from 1:1 to 2:1). In all cases, the same two products were obtained. However, when a large excess of the diketone (5:1) and small volume of the solvent (acetonitrile, *ca.* 50 ml.) were employed, a white precipitate, later shown to be Mn(hfac)$_2$(H$_2$O)$_2$[12] (infrared spectrum), was also isolated from the reaction mixture.

Infrared Spectrum of Mn(CO)$_4$(hfac).—Metal carbonyl stretching frequencies were observed at 2123 (w), 2055 (s), 1973 (s), and 1950 (s) cm.$^{-1}$ (Beckman IR-9; chloroform solution); the ketonic carbonyl stretching frequency at 1635 (s) cm.$^{-1}$ (KBr pellet); the C–H in-plane bend at 1142 (s) cm.$^{-1}$ (KBr pellet); other bands at 3155 (w), 3019 (w), 2952 (w), 2300 (w), 1603 (m), 1570 (sh), 1565 (sh), 1557 (m), 1531 (m), 1469 (s), 1465 (sh), 1373 (w), 1353 (m), 1268 (s), 1254 (s), 1240 (s), 1215 (s), 1107 (sh), 1039 (w), 957 (w), 817 (w), 801 (s), 770 (w), 746 (m), 703 (sh), 683 (s), 668 (w), 636 (sh), 627 (s), 597 (s), 528 (s), 518 (s), 464 (m), and 451 (m) cm.$^{-1}$ (KBr pellet).

Results and Discussion

Hexafluoroacetylacetonatotetracarbonylmanganese(I), stable over long periods of time in air, is a nonelectrolyte in nitromethane. It is readily soluble in chloroform, acetonitrile, ether, and methyl alcohol; sparingly soluble in hexane and carbon tetrachloride; and insoluble in water. The proton magnetic resonance spectrum of the complex consists of a single signal at τ 3.84; the position of the peak supports a chelate attachment of the hexafluoroacetylacetonato group,[13] and

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[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1964.

[2] W. Hieber, *Sitzungsber. Heidelberg Akad. Wiss.*, **3**, 3 (1929); *Chem. Zentr.*, **1**, 2029 (1929).

[3] W. Hieber and G. Bader, *Z. anorg. allgem. Chem.*, **190**, 193 (1930).

[4] acac = anion of pentane-2,4-dione; tfac = anion of 1,1,1-trifluoropentane-2,4-dione; hfac = anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

[5] T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, **2**, 263 (1963).

[6] M. L. Larson and F. W. Moore, *ibid.*, **1**, 856 (1962).

[7] J. C. Goan, C. H. Huether, and H. E. Podall, *ibid.*, **2**, 1078 (1963).

[8] See, for example, R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964), and references therein; also, R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964), and quoted references.

[9] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

[10] E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

[11] It has been our experience that chemical analyses of fluorine-containing compounds often give high hydrogen contents.

[12] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

[13] J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society Washington, D. C., 1963, p. 78.