groups. When ^{13}CO was used in the reaction, CO exchange occurred between the cluster carbonyl and the ^{13}CO reactant but the methane produced was largely $^{12}CH_4$. On the other hand, the use of ^{13}C-enriched trimethyl phosphite produced a mixture of $^{13}CH_4$ and $^{12}CH_4$ in the relative amounts expected from the isotopic distribution in the labeled phosphite.

The use of D_2 in place of H_2 in either the toluene–trimethyl phosphite or the trimethyl phosphite solutions produced predominantly CH_3D and CH_4 in a ratio of ca. 5:1. Lesser amounts of CH_2D_2, CHD_3, and CD_4 were formed in trimethyl phosphite–toluene solutions, and only trace amounts of these species were detected in the trimethyl phosphite solutions. Both HD and H_2 were observed in the D_2 experiments, indicating that extensive hydrogen–deuterium exchange between D_2 gas and the protons of trimethyl phosphite had occurred.

Although no other hydrocarbon products were observed in the reaction system containing trimethyl phosphite, dimethyl ether was produced. In the ^{13}C-enriched trimethyl phosphite reactions, both mono- and di-^{13}C-labeled dimethyl ether was observed in addition to ether with a normal isotopic distribution. When hydrogen was omitted from these reaction systems, methane was still formed but in lower yield ($CH_4{:}Ir_4(CO)_{12} = 2{:}1$).

Analysis of the liquid products by gas chromatography, gas chromatography/mass spectrometry, and proton nuclear magnetic resonance spectroscopy showed that, during the reaction, trimethyl phosphite was rearranged to dimethyl methylphosphonate, $CH_3PO(OCH_3)_2$. The rearrangement was complete at 180 °C after about 100 h but was incomplete after only 20 h and occurred even in the absence of the iridium complex. No other products were detected. Thermal rearrangement of phosphites has been reported to be complete at 400–410 °C after ca. 6 h; no gaseous products were observed.[5] Methane was also formed when the phosphonate was used in place of the phosphite in the hydrogenation reaction system.

Although the results do not define a mechanism for the catalytic formation of methane from trimethyl phosphite, processes that may have been occurring in the reaction systems include (1) methyl group transfer from the phosphite to iridium, (2) hydrogenolysis of the carbon–iridium bond to give methane, (3) exchange of gaseous and coordinated CO, (4) thermal rearrangement of trimethyl phosphite, and (5) hydrogen–deuterium exchange between D_2 gas and the methyl hydrogen atoms of trimethyl phosphite. The last process may occur by inter- or intramolecular metal–ligand hydrogen transfer[6] involving intermediates containing $HIrCH_2OPIr$ or $\mathrm{H\overline{IrP}OCH_2}$ groups.

There is precedence for methyl group migration in reactions of trimethyl phosphite with transition-metal complexes and for cleavage of transition-metal–methyl bonds by hydrogen. Methyl group transfer involving trimethyl phosphite was observed in the reaction of trimethyl phosphite and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ to give $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ and $(\eta^5\text{-}C_5H_5)Mo[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$[7a] and in the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2[P(OCH_3)_3]]_2$ with trimethyl phosphite to give $(\eta^5\text{-}C_5H_5)Cr(CH_3)(CO)_2[P(OCH_3)_3]$ and $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$.[7b] The reaction of $(\eta^5\text{-}C_5H_5)_2Co$ with trimethyl phosphite produced $(\eta^5\text{-}C_5H_5)_2Co_3[P(O)(OCH_3)_2]_6$.[8] Methyl group migration from trimethyl phosphite to an arsenido or antiminido group in Mo and W complexes has also been reported.[9] In a related reaction, thermolysis of $Mn(CO)_2[P(OC_2H_5)_3]_3Br$ gave $Mn_6(CO)[P(O)(OC_2H_5)_2]_9$ with gas (not characterized) evolution.[10] Finally, cleavage of methyl groups has been established in reactions of deuterium with methyl complexes of cobalt, nickel, chromium, and rhodium.[11] The predominant product was CH_3D in each case, but some CH_4 was also formed; CH_2D_2, CHD_3, or CD_4 were not detected.

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Registry No. CO, 630-08-0; H_2, 1333-74-0; $P(OCH_3)_3$, 121-45-9; $Os_3(CO)_{12}$, 15696-40-9; $Ir_4(CO)_{12}$, 18827-81-1; CH_4, 74-82-8; $CH_3PO(OCH_3)_2$, 756-79-6.

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Evidence for a Novel π-Bonded Aquoorganochromium(III) Ion, $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$

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Early attempts to prepare thermally stable σ bonded alkyl and aryl transition-metal complexes were usually successful only if π-bonding ligands such as carbon monoxide were also present. Accordingly, theories were developed that explained these observations on the basis of electronic effects, and these theories were widely accepted. Now it is acknowledged that the role of L in L_nMR complexes is to be a "good ligand" for M and to firmly occupy coordination positions. Thus aquoorganochromium(III) complexes like $(H_2O)_5CrCHCl_2^{2+}$[1,2] are not now considered extraordinary. Similar statements about the role of L in contributing to the electronic stabilization of π-bonded organo transition metal complexes have been made. Indeed, the great majority of complexes with carbon–metal olefinic bonds do have π-acceptor ligands. There are relatively few such complexes with hard ligands such as water or chloride ion.

We wish to report evidence for the existence in acidic aqueous solution of the ion $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ with chromium in the formal +3 oxidation state. To our knowledge there is only one other report[3] of a π-bonded organometallic complex with only waters as the coligands. Comparison of the properties of the $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ ion with results

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from the large body of research on classical chromium(III) aquo coordination complexes promises to shed insight into how a π-bonding ligand can affect the chemistry of complexes.

Experimental Section

Chromocene, $(\eta^5\text{-}C_5H_5)_2Cr$, was prepared by addition of freshly prepared sodium cyclopentadienide to anhydrous chromium chloride in THF under a dinitrogen atmosphere. The crude product was sublimed under vacuum and collected and stored under dinitrogen in a Schlenk tube.

Solutions Containing $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ Ion. Approximately 0.1 g of chromocene was added to 25 mL of ice-cold concentrated perchloric acid, tetrafluoroboric acid, or fresh, glass-distilled trifluoromethylsulfonic acid under a dinitrogen inert atmosphere. The acids had previously been deoxygenated by purging with dinitrogen for 1 h or by undergoing at least four freeze–thaw vacuum cycles. In all cases the solid chromocene dissolved, producing an initial orange-red solution, which quickly became cloudy. A gas was evolved, a dark, gummy substance was precipitated, and the final solution was a deep violet. The gas was identified as dihydrogen by mass spectral analysis. The precipitate was removed either by filtration or by shaking with several aliquots of 1:1 ether–benzene. The solutions with the various acids yielded similar UV–vis spectra.

The compound $NH_4[(\eta^5\text{-}C_5H_5)CrCl_3]$ was synthesized according to the method of Fischer, Ulm, and Kuzel.[4] Identification of this material was by comparison of infrared spectra. A 0.1-g sample of this material (0.41 mmol) was dissolved in 25 mL of concentrated perchloric or tetrafluoroboric acid, and solid silver perchlorate (0.69 g, 0.42 mmol) was added. Immediate precipitation of silver chloride was noted, and the solution rapidly turned from deep blue to violet. The UV–vis spectrum was similar in wavelength maxima and in molar absorbancies to that observed by dissolving solid chromocene in perchloric, hydrofluoroboric, or trifluoromethylsulfonic acid.

A solution of 0.1 g of chromocene in 15 mL of THF was added to a solution of 0.10 g of I_2 (0.41 mmol) in 50 mL of THF. A fast reaction producing a yellow precipitate, $[(\eta^5\text{-}C_5H_5)_2Cr]I$, was observed. This material was filtered in Schlenk-ware under dinitrogen and was then added to 25 mL of cold, deoxygenated perchloric acid. This solution was allowed to stand for 24 h during which a dark, gummy precipitate was formed but no gas evolution was observed. The UV–vis spectrum of the solution was similar to that observed previously.

Isolation of Solid. A 0.1-g sample of chromocene was added to 25 mL of cold, deoxygenated, concentrated tetrafluoroboric acid solution. A dark precipitate was removed by shaking with three 15-mL aliquots of 1:1 ether–benzene. The final violet solution was placed in a Schlenk tube, frozen by liquid dinitrogen, and subjected to vacuum ($\sim 10^{-4}$ mmHg) for 3 days. The sample was kept at the temperature of an isopropyl alcohol–dry ice slush during the lyophilization stage. A dark purple film was observed in the Schlenk tube at the end of this period. This material was taken up in nitromethane and then ether was added to precipitate a violet solid. When dissolved in perchloric acid solution, the violet solid yielded a similar UV–vis spectra to those previously observed. Infrared spectra of the solid were taken in KBr disks and Nujol mulls; yield 0.11 g, 72% based on $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_3](BF_4)_2$. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_3](BF_4)_2$: Cr, 15.09; C, 17.41; H, 3.19. Found: Cr, 16.10; C, 17.94; H, 3.39. Calcd for possible impurity $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_2F](BF_4)_2$: Cr, 20.09; C, 23.12; H, 3.48.

Kinetic Experiments. Solutions containing the proposed $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion in 6 M perchloric acid were prepared and rapidly mixed with hydrochloric and perchloric acid mixtures ($I = 6.0$ M). UV–vis spectra were taken to estimate the concentration of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion prior to mixing. The resultant mixtures were filtered under dinitrogen into a jacketed 0.1-cm cell maintained at 25.0 °C by circulation of thermostated water. Repetitive spectra were taken, and kinetic data were measured until isosbestic points were observed to disappear. Alternatively solid $NH_4[(\eta^5\text{-}C_5H_5)CrCl_3]$ was dissolved in 6 M HCl and then rapidly diluted 5–20-fold with 6 M perchloric acid solutions. The resultant solutions were then filtered under dinitrogen into jacketed cells.

Physical Measurements. Kinetic measurements and UV–vis spectra were obtained on a Cary Model 219 spectrophotometer. Infrared spectra were measured in Nujol mulls or KBr pellets on a Perkin-Elmer Model 283 spectrophotometer.

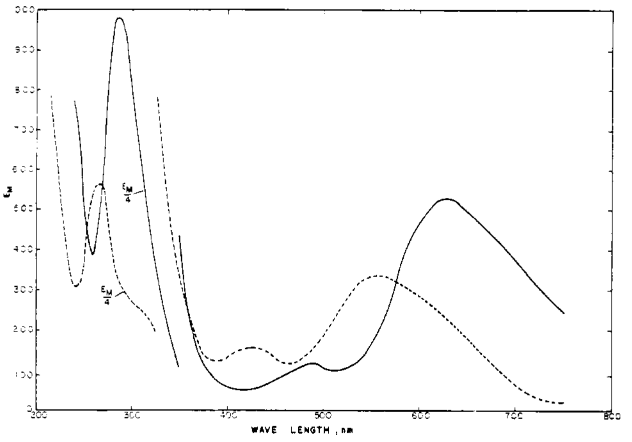

Figure 1. UV–vis spectra of (- - -) $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ ion (6 M $HClO_4$) and (—) $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion (6 M HCl).

Results and Discussion

If chromocene, $(\eta^5\text{-}C_5H_5)_2Cr$, is added to a cold, deoxygenated solution of perchloric acid, a color change from initial orange-red to a final deep violet is noted. There is evolution of a gas, H_2, and the appearance of a tarry precipitate of polymeric cyclopentadiene. The stoichiometry of this reaction can be written as

$$Cr(\eta^5\text{-}C_5H_5)_2 + 2H^+ \xrightarrow[H_2O]{HX} (\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+} + {}^1/_2H_2(g) + C_5H_6$$

The acids $HClO_4$, HBF_4, and CF_3SO_3H, with noncoordinating anions, all yield the same chromium species as judged by identical UV–vis spectra. Fischer et al.[4] have used this same reaction in hydrochloric acid and have isolated a complex with the formula $NH_4[(\eta^5\text{-}C_5H_5)CrCl_3]$.

Other synthetic routes to the aquo complex have proven successful. When silver perchlorate is added to a deep blue solution of $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion, silver chloride precipitates, and the final solution gives the same UV–vis spectrum as that from reactions of chromocene and $HClO_4$. A third method of preparation involves dissolving $[(\eta^5\text{-}C_5H_5)_2Cr]I$ in perchloric acid. Over 24 h the solution turns violet with a concomitant formation of the tarry precipitate but no evolution of a gas. The final UV–vis spectrum of the solution is similar to that obtained from the other syntheses.

The UV–vis spectrum of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_n^{2+}$ exhibits maxima at 550, 425, and 264 nm, while the spectrum of $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion has maxima at 624, 492, and 285 nm. Complete spectra of the aquo and chloro complexes are presented in Figure 1. The two spectra are quite similar, and the blue shift for the aquo species is expected from the relative position of water and chloride ion in the spectrochemical series.

A concentrated solution of the aquo ion in HBF_4 was frozen at liquid nitrogen temperature and submitted to dynamic vacuum for a period of 3 days. The dark violet gummy residue was taken up in nitromethane, concentrated under vacuum, and then a violet solid was obtained by rapidly adding ether. This violet solid yields a UV–vis spectrum similar to Figure 1 when dissolved in perchloric acid. Infrared spectral data of the violet solid are presented in Table I, along with data on Fischer's $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion and ranges from bands expected for π-bonded C_5H_5 metal complexes.[5] The observed bands for both the aquo and chloro complexes fall very nicely within the allowed limits except for expected bands near 1100

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Table I. Infrared Data (cm^{-1}) for π-Bonded Cyclopentadienylchromium Aquo and Chloro Complexes

$[(\eta^5\text{-}C_5H_5)Cr(OH_2)_n](BF_4)_2$	$NH_4[C_5H_5CrCl_3]$	range for $(\eta^5\text{-}C_5H_5)M$[a]
3100	3157	(C-H) 3115-3012
1432	1405	(C-C) 1447-1400
1090[b,c]	1114	(C-H) 1126-1097
	1010	(C-H) 1017-998
838	851	(C-H) 850-712
	839	
	813	

[a] H. P. Fritz, *Chem. Ber.*, 92, 780 (1959). [b] Broad, asymmetric. [c] BF_4^- has a broad band at 1100 cm^{-1}.

cm^{-1}, which are obscured by broad BF_4^- absorption in the aquo complex. We take the infrared data as good evidence that the C_5H_5 ligand is π-bonded in both chloro and aquo complexes; furthermore, the close similarity in UV-vis spectra is evidence that there are three ligands in the coordination sphere of each complex. The solid obtained by lyophilizing HBF_4 solutions gives a low value for percentage of oxygen in the complex, and we suspect that decomposition of the BF_4^- anion has taken place in concentrated acidic medium leading to formation of fluoride ion, which can replace water.

Preliminary experiments on the rates of reactions of the aquo complex have been performed. On standing under nitrogen at room temperature, a light-sensitive, violet solution of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion gradually becomes turbid and its color changes from violet to bluish gray. Finally a dark brown precipitate separates, and the solution exhibits the UV-vis spectrum of $Cr(OH_2)_6^{3+}$ ion. The first turbidity is apparent to the eye after 1 h, but fluctuating spectrophotometric readings occur before this. In several experiments freshly prepared solutions of the aquo complex were filtered under dinitrogen to remove the polymeric cyclopentadiene and then placed in jacketed spectrophotometric cells (25 °C). Repetitive visible spectra were then taken. Isobestic points, which persisted for about 25 min, were observed at 524 and 342 nm. Approximate values of rate constants were obtained by applying the Guggenheim method[6] to absorbance vs. time data measured before the loss of the isobestic points. A value of 1×10^{-2} s^{-1} for the replacement of the cyclopentadiene ligand was obtained (25 °C, 6 M $HClO_4$). In the other experiments, freshly prepared solutions of $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion in 6 M$HClO_4$ were mixed with solutions (I = 6.0 M) that contained chloride ion. When the final solution had a high concentration of chloride ion, (5 M), a rapid color change from violet to blue was noted, and the UV-vis spectrum 5 min after mixing was very similar to that of $(\eta^5\text{-}C_5H_5)CrCl_3^-$ ion. In other experiments, freshly prepared solutions of the aquo complex were first filtered to remove polymeric cyclopentadiene and then absorbancies were measured at several wavelengths so that the concentration of the complex could be estimated. A solution that contained HCl and $HClO_4$ (I = 6.0 M) was then prepared so that on mixing, the final solution would contain equal concentrations of the aquo complex and chloride ion. In one typical experiment, the final concentrations were 3.5×10^{-3} M. Even under these low concentration conditions the spectral changes were too rapid to allow accurate determination of rate constants. The UV-vis spectrum 5 min after mixing exhibited maxima at 567 and 430 nm. This represents a red shift of 17 nm for the low-energy maximum and 5 nm for the higher energy and is consistent with the replacement of water by chloride ion in the inner coordination sphere of chromium. It is reasonable to assume that under low concentration conditions the reaction is

$$(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+} + Cl^- \rightarrow (\eta^5\text{-}C_5H_5)Cr(OH_2)_2Cl^+ + H_2O$$

From the data we have obtained, a reasonable lower limit for the second-order rate constant for this reaction is 10 M^{-1} s^{-1} (T = 25 °C, I = 6.0 M, $[H^+]$ = 6.0 M). This value is much larger than rate constants for substitution reactions in classical chromium(III) coordination complexes.

Further kinetic studies on reactions of the $(\eta^5\text{-}C_5H_5)Cr(OH_2)_3^{2+}$ ion are planned, and a stopped-flow apparatus is under construction.

Acknowledgment. L.O.S. thanks the donors of the American-Swiss Foundation for partial support. Special thanks go to Professor Helmut Werner for many helpful discussions and for generous use of his laboratory facilities at the University of Zurich.

Registry No. $[(\eta^5\text{-}C_5H_5)Cr(OH_2)_3](BF_4)_2$, 78764-13-3; $NH_4[(\eta^5\text{-}C_5H_5)CrCl_3]$, 78764-14-4; $(\eta^5\text{-}C_5H_5)_2Cr$, 1271-24-5; Cl^-, 16887-00-6.

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Formation and Decomposition of Thiosulfate in the Ferrous Sulfide-Sulfur Dioxide Reaction

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In a series of recent publications, Thom et al.[1-4] proposed a mechanism for the formation of elemental sulfur during the reaction of FeS with aqueous solutions of SO_2 which can be represented by the overall equation (1). In this mechanism,

$$FeS + 2SO_2(aq) \rightarrow FeSO_4 + {}^1/_4S_8 \qquad (1)$$

these authors proposed that SO_2 is first adsorbed on the FeS surface, which subsequently results in the formation of ferrous iron and thiosulfurous acid as shown in eq 2 and 3. This acid

$$FeS + SO_2(aq) \rightarrow FeS{\cdot}SO_2(ads) \rightarrow Fe^{2+} + S_2O_2^{2-} \qquad (2)$$

$$S_2O_2^{2-} + 2H^+ \rightarrow H_2S_2O_2 \qquad (3)$$

then reacts with HSO_3^- to form thiosulfate which then reacts with the sulfoxylate anion to form disulfanedissulfonic acid (eq 4 and 5). Through a series of consequetive reactions,

$$H_2S_2O_2 + HSO_3^- \rightarrow H_2S_2O_3 + HSO_2^- \qquad (4)$$

$$H_2S_2O_3 + HSO_2^- \rightarrow HO_3SS{\cdot}SOH + OH^- \qquad (5)$$

finally elemental sulfur is formed according to eq 6.

$$HS_8{\cdot}SO_3^- \rightarrow S_8 + HSO_3^- \qquad (6)$$

The authors studied this reaction by adding FeS or other sulfide to a solution of Na_2SO_3 in a closed vessel and then by acidifying by HCl to generate SO_2 which then attacks the sulfide. The reaction was monitored by recording the change in pressure and analyzing samples periodically for Fe^{2+},$S_2O_3^{2-}$ ions. The experimental conditions, however, are ill-defined because, depending on the amount of HCl added, the following species will all be present: SO_3^{2-}, HSO_3^-, and SO_2. In all tests,

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