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The HCr(CO)$_5^-$ Anion

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The hydridochromium pentacarbonyl anion, HCr(CO)$_5^-$, has been isolated and spectroscopically defined as its Et_4N^+ and Ph_4As^+ salts. Its great tendency to bind to transition-metal Lewis acids such as [M(CO)$_5^0$] (M = Mo, W) and [Mo(PPh$_3$)(CO)$_4^0$] has allowed for an efficient clean synthesis of heterobinuclear bridging hydride complexes.

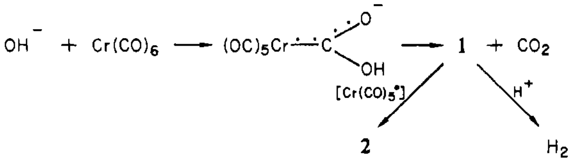
Introduction

In 1957 Behrens and Weber[1] reported the protonation of Cr(CO)$_5^{2-}$ by an aqueous solution of tris(*o*-phenanthroline)iron(II) sulfate, thus isolating [Fe(*o*-phen)$_3$][HCr(CO)$_5$]$_2$. The analytically pure, crystalline salt was chemically characterized only by its reaction with water, yielding H_2 and [Cr(CO)$_5^0$], which, according to eq 1, is scavenged by HCr(CO)$_5^-$, yielding the quite stable (μ-H)[Cr(CO)$_5$]$_2^-$. This bridging hydride, **2**, constitutes a thermodynamic sink in the descriptive chemistry of group 6B carbonyl anions.

$$\underset{\mathbf{1}}{HCr(CO)_5^-} + [Cr(CO)_5^0] \rightarrow \underset{\mathbf{2}}{(\mu\text{-H})[Cr(CO)_5]_2^-} \qquad (1)$$

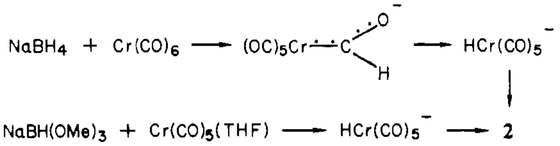
Although the HCr(CO)$_5^-$ anion is suspicioned to be present in reactions resulting in reduction of Cr(CO)$_6$ via nucleophilic addition, eq 2–4, the lack of definite spectroscopic identification has hampered clarification of its mechanistic role. In all of the processes shown here, generally carried out at temperatures >65 °C, where at least some CO dissociation from Cr(CO)$_6$ occurs, the bridging hydride carbonylate was the ultimate and predominant product; however, infrared monitors suggested intermediates prior to the formation of **2**.

water-gas shift reaction[2]



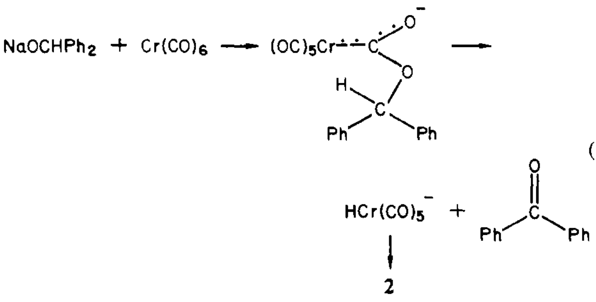
(2)

reduction by hydride[3,4]



(3)

reduction by alkoxides[4]



(4)

To redress this neglect of the mononuclear hydride, we have isolated and spectroscopically defined HCr(CO)$_5^-$ as its Et_4N^+ and Ph_4As^+ salts. Studies of its reaction chemistry have thus far focused on its great tendency to bind to transition-metal Lewis acids such as [M(CO)$_5^0$] and [M′(CO)$_5^+$]. With M = Mo and W an efficient, clean synthesis of mixed-metal dimeric complexes was effected.

Experimental Section

All reactions and transfers were carried out with rigorous exclusion of O_2 and moisture, making use of Schlenk techniques and an Ar-filled glove box. Solvents were purified as specified and degassed by freeze–thaw techniques prior to use. Infrared spectra were recorded in matched, sealed 0.1-mm NaCl cells on a Perkin-Elmer 283B or 521 spectrophotometer. Calibration was against Mo(CO)$_6$ in hexane; ν(CO) = 1989.1 cm^{-1}. Proton (90 MHz) and carbon-13 (15.03 MHz) NMR measurements were taken on JEOL FX90Q and FX60 instruments, respectively.

Materials. Tetrahydrofuran was distilled from 0.1 M Na/Ph$_2$C=O under N_2. Acetonitrile was stirred over CaH$_2$, refluxed and distilled from P_2O_5, and stored over and collected by distillation from CaH$_2$. Methanol was dried over molecular sieves and freeze–thaw degassed. Hexane was stirred over concentrated H_2SO_4 overnight, washed with aqueous NaHCO$_3$ and pure water several times, and dried over CaSO$_4$. Following reflux over and distillation (under N_2) from CaH$_2$, the hexane was degassed by freeze–thaw methods. Cr(CO)$_6$ was purchased from Strem Chemicals and used without purification. The labile ligand complexes, Mo(CO)$_5$pip (pip = piperidine),[5] W(CO)$_5$pip,[5] Mo(CO)$_4$(PPh$_3$)pip,[6] and Mn(CO)$_5$(NCCH$_3$)$^+$PF$_6^-$ [7] were prepared according to published procedures.

Synthesis of Et_4N^+HCr(CO)$_5^-$. Reduction of Cr(CO)$_6$ by Na^0 in liquid ammonia was carried out according to the method of Behrens[1] as modified by Ellis.[8] A convenient scale for the synthesis was 7.5 g of Cr(CO)$_6$ (0.034 mol), 2.8 g of Na^0 (0.122 mol), and 250 mL of liquid NH$_3$ predried by trap to trap distillation from Na^0. Filtration and transfer of the NH$_3$ solution of Na$_2$Cr(CO)$_5$ was most readily accomplished by a cannula, fitted via septum cap with a fritted disk which was immersed in the reaction medium. By this method most of the Na$_2$(CO)$_2$ (pyrophoric and explosive) and NaNH$_2$ remained in the reaction flask, which was later defused with absolute EtOH, with *much caution*. The Na$_2$Cr(CO)$_5$ thus obtained was recrystallized from THF (ca. 7.0 g of [Na(THF)$_x$]$_2$Cr(CO)$_5$) and stored in the drybox. Since the value of x in the THF solvate is uncertain ($1 \lesssim x \lesssim 2$), an exact yield could not be calculated.

To 2.45 g of [Na(THF)$_x$]$_2$Cr(CO)$_5$ in 50 mL of CH$_3$CN was added 1.5 mL of MeOH, causing the immediate formation of yellow HCr(CO)$_5^-$ and precipitation of NaOMe. Following filtration (fine-porosity frit), a solution of 3.7 g of $Et_4N^+Br^-$ in 10 mL of MeOH was added. Repeated vacuum concentration of the solution followed by addition of THF allowed for the removal of solid NaBr and excess Et$_4$NBr by filtration. When no further precipitates were driven from the solution, the solvent was completely removed, yielding an orange oil which solidified upon trituration with small quantities of hexane; yield 1.0 g of Et_4N^+HCr(CO)$_5^-$. Anal. Calcd for $C_{13}H_{21}O_5CrN$:

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Table I. ν(CO) Infrared and ^{1}H NMR Data for $HCr(CO)_5^-$ and Dimeric Derivatives

compd	ν in THF, cm^{-1}	δ (Me_4Si = 0)
$Et_4N^+HCr(CO)_5^-$	2023 vw, 1892 s, 1860 m	−7.0 (CD_3CN)
$Ph_4As^+HCr(CO)_5^-$	2020 vw, 1889 s, 1860 m	−7.0 (CD_3CN)
$Et_4N^+(\mu\text{-H})[Cr(CO)_5]_2^-$	2033 w, 1946 s, 1886 m	−19.5 (CD_3CN, THF)^a
$Et_4N^+(\mu\text{-H})[Mo(CO)_5]_2^-$	2044 w, 1946 s, 1881 m^a	−12.2 (THF)^a
$Et_4N^+(\mu\text{-H})[W(CO)_5]_2^-$	2041 w, 1941 s, 1879 m^a	−12.6 (THF)^a
$Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_5]^-$	2032 w, 1948 s, 1884 m	−15.47 (CD_3CN)^a
$Et_4N^+(\mu\text{-H})[Cr(CO)_5][W(CO)_5]^-$	2039 w, 1946 s, 1886 m	−15.60 (CD_3CN)^a

^{a} Values are in agreement with those of ref 3.

C, 48.29; H, 6.55; Cr, 16.08. Found: C, 48.43; H, 6.63; Cr, 15.61 (Galbraith Laboratories). The analytically pure sample was recrystallized from THF/hexane. Attempts to isolate the sodium salt by this procedure resulted in decomposition of the resultant $Na^+HCr(CO)_5^-$ oil. The sodium salt was stable only in solution. The Ph_4As^+ salt however was isolated similarly to $Et_4N^+HCr(CO)_5^-$.

Synthesis of Mixed-Metal Bridging Hydride Carbonylates. Stoichiometric amounts of $Et_4N^+HCr(CO)_5^-$ (typically 0.20-g quantities) and $Mo(CO)_5$pip or $W(CO)_5$pip were dissolved in 20 mL of THF and stirred at room temperature for 15 h ($Mo(CO)_5$pip) or 48 h ($W(CO)_5$pip). The solution volume was reduced by half, and, upon addition of hexane, a yellow powder was isolated in >90% yields. Anal. Calcd for $C_{18}H_{21}O_{10}NMoCr$: C, 38.65; H, 3.78; Cr, 9.30. Found: C, 38.46; H, 4.08; Cr, 8.61.

Similarly $Mo(CO)_4(PPh_3)$pip was reacted with $AsPh_4^+HCr(CO)_5^-$ (3–4 h), yielding a yellow oil when driven out of THF solution by hexane.

Attempted Synthesis of (μ-H)[$Cr(CO)_5$][$Mn(CO)_5$]. A 0.20-g quantity of $Et_4N^+HCr(CO)_5^-$ (0.63 mmol) was mixed with 0.25 g (0.66 mmol) of $Mn(CO)_5(NCCH_3)^+PF_6^-$ in 20 mL of THF. (Dissolution of the poorly soluble manganese salt occurred as the reaction proceeded.) The mixture was stirred for 3 h at room temperature followed by vacuum removal of solvent. Both the hexane-soluble extract of the residue as well as the sublimate (50 °C, 0.01 mm) contained $Cr(CO)_6$, $Mn_2(CO)_{10}$, and an unidentified product.

Other Reactions of $HCr(CO)_5^-$. (a) H_2O. To a 2-mL solution of $Et_4N^+HCr(CO)_5^-$ in THF was added 5 mL of degassed H_2O. Although the water drives $Et_4N^+HCr(CO)_5^-$ out as an oil, vigorous shaking for 10 min promotes the two-phase reaction, resulting in the evolution of H_2, identified by gas chromatography, and a yellow crystalline product whose IR spectrum matches that of $Et_4N^+(\mu\text{-H})[Cr(CO)_5]_2^-$.

(b) $Ph_3C^+BF_4^-$. Stoichiometric amounts of Ph_3CBF_4 and $Ph_4As^+HCr(CO)_5^-$ were dissolved in THF. A gas evolved as the insoluble Ph_3CBF_4 reacted with $HCr(CO)_5^-$ to yield $(\mu\text{-H})[Cr(CO)_5]_2^-$. The identity of the gas was not determined.

(c) $Cr(CO)_6$. Stoichiometric amounts of $Ph_4As^+HCr(CO)_5^-$ and $Cr(CO)_6$ were dissolved in a few milliliters of THF. After the mixture was stirred for 15 h at 25 °C, ca. 30% of the mononuclear hydride was converted to $(\mu\text{-H})[Cr(CO)_5]_2^-$.

(d) C_2H_4. No reaction was observed on heating $Et_4N^+HCr(CO)_5^-$ in THF to 50 °C under 1 atm of ethylene with magnetic stirring over 3–4 h.

Results and Discussion

Spectral Properties. The ν(CO) infrared spectrum of $Et_4N^+HCr(CO)_5^-$ is compared to that of the more common $(\mu\text{-H})[Cr(CO)_5]^{2-}$ as well as the mixed-metal carbonylate $(\mu\text{-H})[Cr(CO)_5][Mo(CO)_5]^-$ in Figures 1 and 2. Reflective of a similar local geometry about the metal in each of the anions, spectral *patterns* are substantially similar in the three cases. However, the most intense band, assigned to the E vibrational mode in C_{4v} local symmetry for both the mononuclear and the binuclear species, is over 50 cm^{-1} lower for $HCr(CO)_5^-$ (Table I). Cotton–Kraihanzel force constants[9] for $HCr(CO)_5^-$ have been calculated at k_1(axial CO) = 14.16 and k_2(equatorial CO's) = 15.11 mdyn/Å. The greater values for the analogous force constants of $(\mu\text{-H})[Cr(CO)_5]_2^-$, k_1 = 14.38 and k_2 = 15.66 mdyn/Å, agree with the expectation that the hydridic charge is more dispersed by the two pendant $Cr(CO)_5{}^0$ units of the binuclear anion.

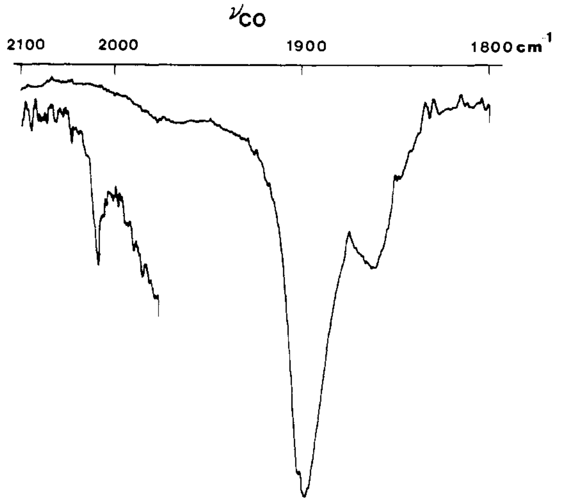

Figure 1. ν(CO) stretching region of the IR spectrum of $Et_4N^+HCr(CO)_5^-$ in THF solution. Overlay is of a highly concentrated solution.

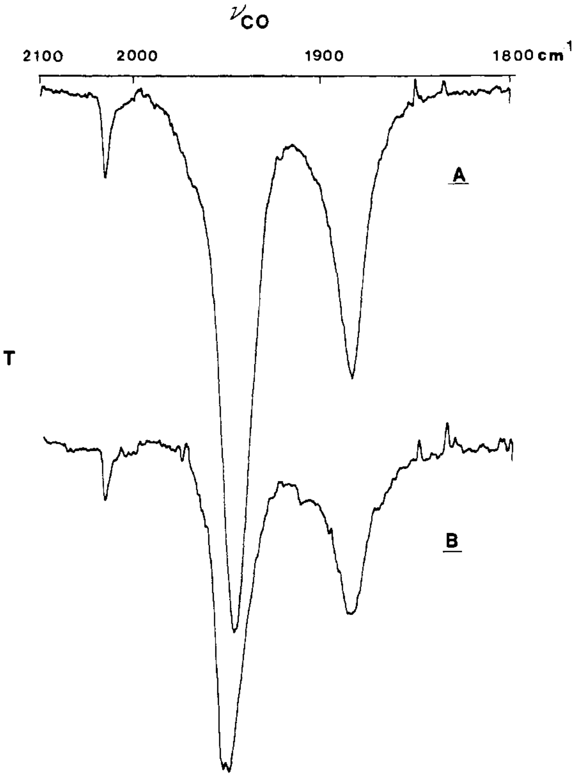

Figure 2. ν(CO) stretching regions of the IR spectra of (A) $Et_4N^+(\mu\text{-H})[Cr(CO)_5]_2^-$ and (B) the mixed-metal bridging hydride $Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_5]^-$ in THF solution.

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An important difference in the ν(CO) IR spectra of $HCr(CO)_5^-$ and $(\mu\text{-H})[Cr(CO)_5]_2^-$ is the very low intensity of the high-frequency $A_1^{(2)}$ band of the former. As in the ν(CO) spectrum of isoelectronic $HMn(CO)_5$,[10] this allowed band (assuming C_{4v} symmetry) is only observed on highly concentrated solutions of $HCr(CO)_5^-$. It is thus likely that $HCr(CO)_5^-$ will be isostructural with $HMn(CO)_5$; i.e., a considerable deviation from octahedral geometry is expected with the $(OC)_{ax}\text{–}Cr\text{–}(CO)_{eq}$ bond angle >90°. This would also be analogous to the structure of C_{3v} $HFe(CO)_4^-$, which has, both in solution[11] and in the solid state,[12] a $(OC)_{ax}\text{–}Fe\text{–}(CO)_{eq}$ angle of ca. 100°. In contrast the carbonyl groups occupy strict octahedral sites about the Cr atoms of $(\mu\text{-H})[Cr(CO)_5]_2^-$, although the hydride itself bridges in a nonlinear manner.[13]

Whereas $HMnCO)_5$ and $HCr(CO)_5^-$ have ^1H chemical shifts at -7.5 and -7.0 ppm upfield from Me_4Si, respectively, that of $(\mu\text{-H})[Cr(CO)_5]_2^-$ is at $\delta = -19.5$. Direct donation of hydride electron density into the carbonyl π^* orbitals *could* contribute to the deshielding of the hydride in the cases of the distorted monomeric complexes relative to the geometrically regular binuclear complex anions. However the predominant influence by far on the hydride nuclear magnetic resonance positions of $HCr(CO)_5^-$ relative to $(\mu\text{-H})[Cr(CO)_5]_2^-$ is expected to be the proximity to the hydride of one transition metal vs. two.

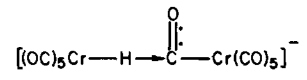
The δ(CO) IR spectra are substantially the same for all homobinuclear and heterobinuclear bridging hydride anions. Fortunately, there is however a large difference in hydride chemical shifts for $(\mu\text{-H})[Cr(CO)_5]_2^-$ ($\delta = -19.5$) and $(\mu\text{-H})[M(CO)_5]_2^-$ (M = Mo, $\delta = -12.2$; M = W, $\delta = -12.6$). The mixed-metal bridging hydrides exhibit resonances at an average value (Table I), which readily permits identification of the heterobinuclear anions.

Chemical Reactivity. Attempts to isolate $HCr(CO)_5^-$ from the reaction of a hydride-donating main group reagent (such as $BH(OMe)_3^-$ or KH) with photochemically generated $THF\cdot Cr(CO)_5$ yielded only $(\mu\text{-H})[Cr(CO)_5]_2^-$ in our hands.[4] This propensity of the $HCr(CO)_5^-$ anion to form strong adducts with transition-metal Lewis acids has been used to effect a simple and high-yield (>90%) synthesis of the mixed-metal bridging hydrides, $Et_4N^+(\mu\text{-H})[Cr(CO)_5][W(CO)_5]^-$ and $Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_5]^-$. (The available synthesis of such salts generates mixtures of the homo- and heterobinuclear anions.[3]) The procedure made use of $LMo(CO)_5$ and $LW(CO)_5$ where L = piperidine, a ligand whose ready lability allowed for the thermal generation of $M(CO)_5^0$ fragments at temperatures where thermal decomposition of derived $(\mu\text{-H})[Cr(CO)_5][M(CO)_5]^-$ was not problematical.[3]

A phosphine-substituted heterobinuclear bridging hydride, $Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_4PPh_3]^-$, was similarly prepared by reaction of $Et_4N^+HCr(CO)_5^-$ with $Mo(CO)_4(PPh_3)pip$. The complex ν(CO) IR spectrum of this carbonylate was very similar to that of $Et_4N(\mu\text{-H})[Mo(CO)_5][Mo(CO)_4PPh_3]^-$. For the latter anion, an X-ray structure analysis established that the PPh_3 group was cis to the μ-H bridge and exo to the bent molecular framework, $(OC)_{ax}\text{–}Mo\text{–}Mo'\text{–}(CO)_{ax}$.[14]

Attempts to prepare $(\mu\text{-H})[Cr(CO)_5][Mn(CO)_5]$ via the labile ligand technique ($HCr(CO)_5^- + (CH_3CN)Mn(CO)_5^+$) resulted in the production of $Mn_2(CO)_{10}$, $Cr(CO)_6$, and a hexane-soluble, unidentified compound. These results are similar to those of Graham and co-workers, who attempted to prepare the same molecule by protonation of the metal–metal bond of $[(OC)_5Cr\text{–}Mn(CO)_5]^-$.[15] Since the $(OC)_5W\text{–}H\text{–}Re(CO)_5$ compound was found to be more stable than the light metal analogue, attempts are being made to synthesize this one via reaction of $HW(CO)_5^-$ and $(CH_3CN)Re(CO)_5^+$.

The reaction of $HCr(CO)_5^-$ with $Cr(CO)_6$ at ambient temperatures to yield $(\mu\text{-H})[Cr(CO)_5]_2^-$ is quite slow; nevertheless some product is observed over the course of a day. Although CO exchange in $HCr(CO)_5^-$ is rapid, CO dissociation from $Cr(CO)_6$ is slower than the production of **2**. Condensation of the two components poses an interesting mechanistic question. The intermediacy of a nucleophilic hydride-attack adduct such as **3** is a possibility consistent with known reactivity patterns of transition-metal carbonyl and main-group hydride reagents.[16,17]



$$[(OC)_5Cr\text{—}H\rightarrow\overset{\overset{O}{\|}}{C}\text{—}Cr(CO)_5]^-$$

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Note Added in Proof. A room-temperature X-ray crystallographic analysis of the Ph_4P^+ salt of $HCr(CO)_5^-$ has been carried out by the Crystalytics Co. and refined to $R_F = 3.9$. The anion is of approximate octahedral symmetry with angles substantiating the infrared analysis presented above. Details of the structure will be submitted separately.

Registry No. $Et_4N^+HCr(CO)_5^-$, 77110-93-1; $AsPh_4^+HCr(CO)_5^-$, 77110-94-2; $Et_4N^+(\mu\text{-H})[Cr(CO)_5]_2^-$, 16924-36-0; $Et_4N^+(\mu\text{-H})[Mo(CO)_5]_2^-$, 12082-98-3; $Et_4N^+(\mu\text{-H})[W(CO)_5]_2^-$, 12083-01-1; $Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_5^-$, 77123-43-4; $Et_4N^+(\mu\text{-H})[Cr(CO)_5][W(CO)_5]^-$, 77110-96-4; $Et_4N^+(\mu\text{-H})[Cr(CO)_5][Mo(CO)_4PPh_3]^-$, 77110-98-6; $Mo(CO)_5pip$, 19456-57-6; $W(CO)_5pip$, 31082-68-5; $Mo(CO)_4PPh_3(pip)$, 38780-82-4; H_2O, 7732-18-5; $Ph_3C^+BF_4^-$, 341-02-6; $Cr(CO)_6$, 13007-92-6; $Na_2Cr(CO)_5$, 52154-81-1.

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