studies, particularly those of compound II, strongly suggest that photochemical fragmentation processes can be effectively inhibited by the presence of certain bridging ligands, and ligand substitution reactions become important.

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Registry No. I, 23733-19-9; II, 88746-45-6; III, 84647-91-6; IV, 38979-82-7; V, 88825-32-5; VI, 72282-40-7; VII, 76000-21-0; VIII, 86437-18-5; IX, 86437-19-6.

Supplementary Material Available: A table of structure factor amplitudes is available for the crystal structure analysis (10 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of a Polynuclear Chromium Tetraanion, Tetrakis((μ_3-methoxo)tricarbonylchromate(0))

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Reaction of $Cr(CO)_6$ with excess hydroxide ion in refluxing methanol yields a polynuclear chromium tetraanion, $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$, isolated as its R_4N^+ (R = Me, Et) salt. The X-ray structure of $[Et_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]$ has been determined; the crystals are orthorhombic, space group *Fddd* (D_{2h}^{24}), $Z = 8$, with unit cell dimensions $a = 12.766$ (4), $b = 23.694$ (7), and $c = 38.601$ (12) Å. The anion consists of a distorted cubic A_4B_4 (A = chromium, B = oxygen) arrangement with triply bridging μ_3-methoxide groups and $Cr(CO)_3$ units. A nonbonding Cr–Cr distance of 3.31 (6) Å (average) is consistent with a closed-shell metal configuration. $Cr(CO)_3(CH_3CN)_3$ is formed as the exclusive product when $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ is treated with HCl in acetonitrile. Addition of the tetraanion to concentrated ammonium hydroxide quantitatively yields $Cr(CO)_3(NH_3)_3$.

Introduction

Reactions of the group 6B metal hexacarbonyls with hydroxide ion have received considerable attention owing to the ability of these solutions to catalyze the water gas shift reaction.[2] Depending upon reaction conditions, it has been noted that reaction of $Cr(CO)_6$ with base yields $HCr(CO)_5^-$ and $(\mu\text{-}H)Cr_2(CO)_{10}^-$,[3] as well as other, structurally uncharacterized, polynuclear carbonyl metalates.[4] These metalates, isolated from $KOH/Cr(CO)_6$ reaction mixtures in protic solvents, such as methanol, were believed to be binuclear anions with bridging hydroxo and methoxo groups and containing CO, OH^-, and CH_3OH as ligands.

In comparison, a few related polynuclear carbonyl complexes of molybdenum and tungsten have been characterized. In these complexes rather long M–M distances are consistent with the absence of direct metal–metal bonding. The structure of $[W_2(\mu\text{-}OH)_3(CO)_6]^{3-}$,[5] a product of the alkaline hydrolysis of $W(CO)_6$, consists of two $W(CO)_3$ fragments bridged by three hydroxo groups. Hieber's acid, $[HM(CO)_3(\mu_3\text{-}OH)]_4$ (M = Mo, W),[6] is a tetrahedral array of $M(CO)_3$ units (structurally characterized for the W derivative) with triply bridging OH groups. The neutral adduct, $[Mo(CO)_2(NO)(\mu_3\text{-}OH)]_4$,[7] prepared from the molybdenum derivative of Hieber's acid by replacement of one CO at each metal atom by a nitrosyl group, also contains μ_3-OH bridges. Unusual trimeric species with both doubly and triply bridging ligands are known, $[Mo_3(CO)_6(NO)_3(\mu\text{-}OCH_3)_3(\mu_3\text{-}OCH_3)]^{-}$[8] and $[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]^{3-}$;[9] the tungsten anion is noteworthy in that it is believed to contain a W–W bond on the basis of bond length and the 18-electron requirement.

We now wish to report the synthesis, spectral, and X-ray structural characterization of a polynuclear chromium tetraanion, $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$, a species isolated as its R_4N^+ (R = Me, Et) salt from the reaction of $Cr(CO)_6$ and excess hydroxide ion in methanol. Procedures for the efficient syntheses of $Cr(CO)_3(CH_3CN)_3$ and $Cr(CO)_3(NH_3)_3$ from this polynuclear tetraanion are also presented.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert atmosphere chamber under prepurified argon. All solvents were purified by distillation under nitrogen prior to use. Acetonitrile and methanol were distilled from calcium hydride, tetrahydrofuran from lithium aluminum hydride. IR spectra were obtained on a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer or Varian HFT-80 spectrometer. ^{13}C NMR spectra were obtained with a Bruker HFX-90 spectrometer. All NMR data are listed in ppm relative to internal Me_4Si. GC analyses were performed with a Gow-Mac 69-100 gas chromatograph using a 4 ft × $^1/_4$ in. stainless-steel column packed with Carbowax 20M. Chromium hexacarbonyl was purchased from Pressure Chemical Co., tetramethylammonium hydroxide (20% (w/w) in MeOH) from Alfa Products. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

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$[Et_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]$ (1). To $Cr(CO)_6$ (5.0 g, 0.023 mol) in a 250-mL Schlenk tube equipped with a stir bar was added 25% (w/w) Et_4NOH (40.6 g, 0.069 mol OH^-) in methanol. Approximately 60 mL of dry methanol was added to the reaction flask via cannula. The Schlenk tube was then fitted with a reflux condenser and stopcock. With stirring, the reaction mixture was heated at approximately 50 °C for 6 h, in order to prevent accumulation of volatile $Cr(CO)_6$ in the neck of the condenser. During this time, the solution developed a deep red color. The temperature was increased to methanol reflux, and immediately an orange precipitate began to form. Following overnight reflux, the product was isolated as an orange solid by filtration under inert atmosphere, washing with a 50/50 THF/MeOH solution, and vacuum drying. Recrystallization from hot CH_3CN/THF yielded 4.8 g (71%, based on $Cr(CO)_6$) of 1. An analytical sample was prepared by double recrystallization from CH_3CN/THF: ^1H NMR (CD_3CN) δ 4.21 (s, 3 H, μ_3-OCH_3) 3.28 (q, 8 H, NCH_2), 1.29 (t of t, 12 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 238.0 (Cr–CO), 76.1 (μ_3-OCH_3), 53.1 (NCH_2), 7.8 (NCH_2CH_3); IR (ν(CO), CH_3CN) 1863 (s), 1720 (vs) cm^{-1}.

Anal. Calcd for $C_{12}H_{23}CrNO_4$: C, 47.94; H, 7.89. Found: C, 47.96; H, 8.06.

$[Me_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]$ (2). The above procedure was used for the synthesis of 2 with the following modifications and observations. A 3-fold excess (31.4 g, 0.069 mol OH^-) of 20% (w/w) Me_4NOH in methanol to $Cr(CO)_6$ (5.0 g, 0.023 mol) was used. The reaction mixture developed a deep red color with heating at 50 °C for 30 min, and following 1 h of heating at methanol reflux, the orange-red precipitate so formed was isolated in the manner described above. Recrystallization from hot CH_3CN gave 2: yield 4.2 g, 76%, based on $Cr(CO)_6$; ^1H NMR (CD_3CN) δ 3.34 (s, 3 H, μ_3-OCH_3), 3.24 (s, 12 H, NCH_3); IR (ν(CO), CH_3CN) 1861 (s), 1750 (vs), 1720 (vs), (ν(CO), Fluorolube mull) 1865 (s), 1720 (vs, br) cm^{-1}.

Anal. Calcd for $C_8H_{15}CrNO_4$: C, 39.83; H, 6.28. Found: C, 39.93; H, 6.17.

Synthesis of $Cr(CO)_3(NH_3)_3$ from 2. A sample of 2 (5.0 g, 5.25 mmol) was added to 100 mL of concentrated ammonium hydroxide. The mixture was stirred under argon for 3 h, resulting in a color change from a murky brown to yellow, with formation of bright yellow crystals. The product was washed with 3 × 25 mL portions of concentrated NH_4OH, and dried in vacuo: yield 3.6 g (91%); IR (ν(CO), CH_3CN) 1911 (s), 1778 (vs) cm^{-1}; mp 102 °C dec (lit.[10] 100–105 °C).

Synthesis of $Cr(CO)_3(CH_3CN)_3$ from 2. A sample of 2 (5.0 g, 5.25 mmol) was dissolved in 50 mL of CH_3CN under argon. With stirring, concentrated hydrochloric acid (1.75 mL, 21.0 mmol) was added dropwise into the solution, resulting in a color change from red to bright yellow, with precipitation of Me_4NCl. Concentration in vacuo to a solution volume of approximately 20 mL caused complete precipitation of the salt. Filtration of the reaction solution through a celite pad using standard airless ware techniques, followed by a 3-mL washing of the pad with CH_3CN and evaporation of the solvent, under reduced pressure, gave $Cr(CO)_3(CH_3CN)_3$: yield 5.2 g (96%); IR (ν(CO), CH_3CN) 1918 (s), 1792 (vs) cm^{-1}; ν(CO) pattern identical with that of an authentic sample.[11]

Synthesis of $[Et_4N][Cr(CO)_5Br]$ from 1. A sample of 1 (1.8 g, 1.5 mmol) was added to 50 mL of THF in a 100-mL Schlenk tube. The reaction slurry was saturated with carbon monoxide, and, with stirring, allyl bromide (0.53 mL, 6.1 mmol) was added dropwise with a syringe. The solution slowly developed a yellow color over a 24-h period at room temperature. GC analysis of the solution phase showed allyl methyl ether, by comparison with an authentic sample. The reaction mixture was filtered through a medium-porosity frit. Removal of the volatiles under reduced pressure gave $[Et_4N][Cr(CO)_5Br]$: yield 1.1g (81%); IR (ν(CO), THF) 2053 (w), 1909 (s), 1871 (m) cm^{-1}; lit.[12] ν(CO) 2058 (w), 1906 (s), 1875 (m) cm^{-1}.

Reaction of $Cr(CO)_6$ with Methanolic KOH. A mixture of $Cr(CO)_6$ (2.25 g, 10.2 mmol), KOH (3.8 g, 67.7 mmol), and 60 mL of MeOH was heated at steam-bath temperature for 3 h in a stainless-steel Whitey bomb. Upon cooling, the reactor was vented. Filtration of the product mixture under argon gave 1.8 g of orange solid: IR (ν(CO), Nujol mull) 1860 (s), 1695 (vs, br) cm^{-1}. The solid was added to a solution of 1.5 g of Et_4NBr in 30 mL of CH_3CN and the mixture was allowed to stir overnight. An IR spectrum of the resulting orange-red solution was identical with that of 1.

X-ray Structure Determination. Clear orange crystals without well-defined faces were obtained by slow vapor diffusion of THF into a solution of 1 in CH_3CN. A number of these were cemented with cyanomethacrylate cement in 0.3-mm diameter glass capillaries and sealed under argon. All crystals were of poor diffraction quality. One of these was mounted on a Supper No. 455 goniometer and centered optically on a Syntex $P2_1$ diffractometer. Most operations were carried out as described previously;[13] other operations are described below. Details of the structure analysis, in outline form, are presented in Table I. The structure was solved by the heavy-atom technique utilizing the Patterson function and successive difference Fourier syntheses. Anisotropic thermal parameters for Cr, C, and O atoms in the tetraanion, and isotropic thermal parameters for all non-hydrogen atoms in the cation were used. Two symmetry-independent tetraethylammonium ions are present in the unit cell, each with crystallographic 2 (C_2) symmetry. The α-carbon atoms of the ethyl groups of one of these cations are disordered. This disorder was resolved and the two observed configurations were assigned occupancy factors of 0.5 based on electron density syntheses. One of the disordered configurations is very similar to that found for the ordered cations, while the other is quite different. This disorder is quite similar to that observed in tetraethylammonium chloride monohydrate.[14] Tables containing (1) the isotropic temperature factors and (2) bond lengths and angles for each cation are available as supplementary material. Figures depicting the structure of the ordered cation and each conformation of the disordered cation are also available as supplementary material.

Results and Discussion

Preparation and Structure of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$. A mixture of $Cr(CO)_6$ and Et_4NOH in a 1:3 mole ratio in refluxing methanol gave an insoluble orange compound. An acetonitrile solution of this complex showed a two-band pattern in the infrared carbonyl region (ν(CO) 1863 (s), 1720 (vs) cm^{-1}) suggestive of the presence of a $Cr(CO)_3$ fragment. A ^1H NMR (acetonitrile-d_3) spectrum of the complex exhibited three resonances integrating in the ratio of 12:8:3; two of these peaks could be assigned to the tetraethylammonium cation, and the third to that of a methoxide group.

In order to characterize this species more fully, we investigated its chemical reactivity with a variety of reagents. The results are shown in Figure 1. Briefly, $Cr(CO)_3(CH_3CN)_3$ is formed in 96% yield when the complex is treated with HCl in CH_3CN. Reaction with concentrated ammonium hydroxide yielded $Cr(CO)_3(NH_3)_3$, quantitatively, and a carbon monoxide saturated slurry of the compound in THF reacted with allyl bromide producing $Cr(CO)_5Br^-$ and allyl methyl ether. This complex and the analogous Me_4N^+ salt, which can be conveniently prepared in good yield within a 2-h reaction period, are both soluble in CH_3CN but insoluble in CH_2Cl_2, alcohols, and ethereal solvents. On the basis of the above results, we tentatively formulated the metal-containing species as $[Cr(CO)_3(OCH_3)]_n^{n-}$. Recently, a compound of the general formula $[Et_4N]_n[Cr(CO)_3(OCH_3)]_n$ was prepared from $Cr(CO)_3$(PMTA) (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) and methoxide ion.[9] A cubane-like (n = 4) struc-

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Table I. Summary of the X-ray Diffraction Study of $[Et_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]$

(A) Crystal Data

cryst system: orthorhombic	$Z = 8$
space group: *Fddd* (D_{2h}^{24}, no. 70)	cryst size: 0.34 × 0.34 × 0.63 mm
$a = 12.766\ (4)$ Å	cryst shape: irregular
$b = 23.694\ (7)$ Å	fw = 1189.4
$c = 38.601\ (12)$ Å	d(calcd) = 1.35 g cm^{-3}
$V = 11675.3$ Å^3	d(obsd)^a = 1.33 g cm^{-3}
	$\mu = 8.3$ cm^{-1}

cell constant determination: 12 pairs of ±(*hkl*) and refined 2θ, ω, χ values in the range 23° < $|2\theta|$ < 25° ($\lambda_{MoK_\alpha} = 0.71073$ Å)

(B) Measurement of Intensity Data

radiation	Mo K_α (graphite monochromator)
reflcns measd	$+h, +k, +l$ (to $2\theta = 42°$)
scan type, speed	θ-2θ, variable, 1.95-3.91 min^{-1}
scan range	symmetrical, 0.95° below the K_{α_1} peak and above the K_{α_2} peak
bkgd meas	stationary for $^1/_4$ of the scan time at each of the scan limits
no. of reflcns measd	1583, 1017 with $F > 3.92\sigma(F)$
absorption correction	empirical, transmission factors 0.808-1.000
std reflcns	062; 0, 2, 22; 715, measd after each 50 reflcns
automatic recentering	after every 800 reflcns

(C) Treatment of Intensity Data

data reduction	intensities as before,^{b} esds of F_o values calcd by method of finite differences^c
statistical information^d	$R_s = 0.031$

(D) Refinement,^{e} with 1017 Data for Which $F > 3.92\sigma(F)$

weighting of reflcns	as before,^{b} $p = 0.04$
full-matrix least-squares	anisotropic temperature factors for Cr, C, O atoms in tetraanion, isotropic temperature factors for N, C atoms in cations; $R = 0.086$; $R_w = 0.107$
structure factor calculation, all 1583 data	$R = 0.132$; $R_w = 0.113$
std dev of an observation of unit weight (SDU)	1.969
final difference fourier	5 peaks 0.50-0.70 e$^-$/Å^3 near tetraethylammonium cations, 8 peaks 0.40-0.50 e$^-$/Å^3 again near tetraethylammonium cations; other features random and ⩽ 0.37 e$^-$/Å^3
weighting scheme analysis	no systematic dependence on magnitude of $|F_o|$, (sin θ)/λ, or indices

[a] Flotation method in bromoform/hexane. [b] See ref 13. [c] See ref 25. [d] $R_s = \Sigma(|F_o|)/\Sigma|F_o|$. [e] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; SDU = $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]$, where m (= 1017) is the number of observations and n (= 126) is the number of parameters.

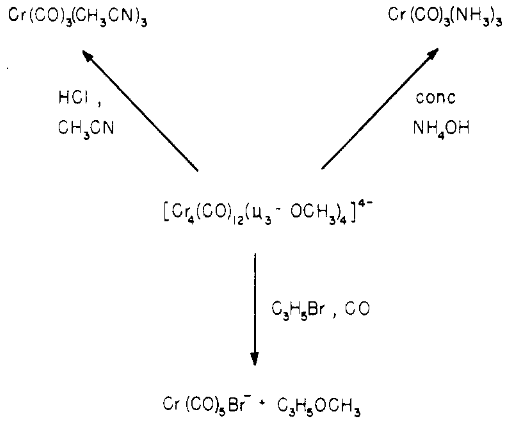

Figure 1. Reactivity of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$.

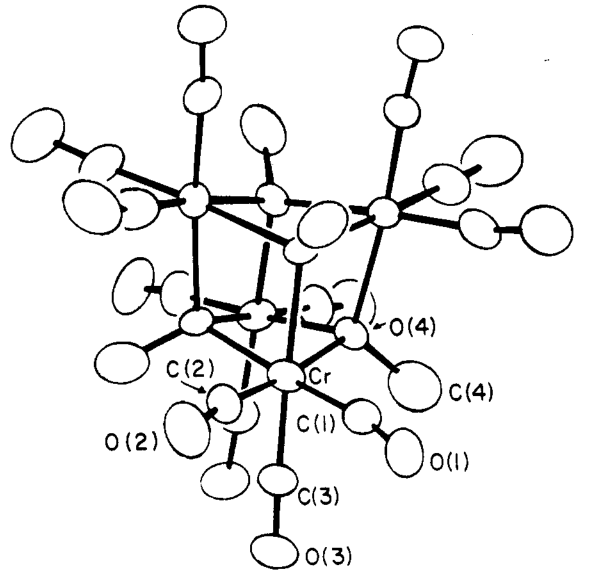

Figure 2. Structure of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ with 222 (D_2) symmetry. Thermal ellipsoids show 50% probability levels.

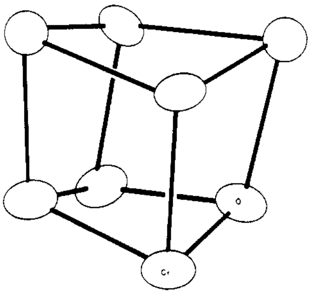

Figure 3. Structure of the Cr_4O_4 core.

ture with face-bridging alkoxide groups similar to that proposed for $[Mn(CO)_3(OCH_2Ph)]_4$[15] was favored on the basis of spectroscopic data. It was noted, however, that attempts to isolate species from reactions containing OH^- and $Cr(CO)_3$(PMTA) were unsuccessful.

Suitable crystals for an X-ray diffraction study of the Et_4N^+ salt were obtained from a CH_3CN/THF solution. The structure of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ is shown in Figure 2. The tetraanion has a cubane-like structure consisting of four $[Cr(CO)_3(OCH_3)]^-$ monomers. The Cr_4O_4 core, shown in Figure 3, is a distorted cube in which the chromium and methoxide oxygen atoms occupy alternate corners. Each Cr(0) atom is six-coordinate, with three coordination sites occupied by terminal CO ligands and the other three sites by O atoms of the methoxide groups. Each μ_3-oxygen atom is four-coordinate, approximately tetrahedral, and bonded to three chromium atoms and a methyl group. Selected bond distances and angles are presented in Table II. Atomic coordinates for all nonhydrogen atoms are listed in Table III. Anisotropic tem-

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Table II. Selected Bond Distances (Å) and Angles (deg)[a] for $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$

Cr-Cr	3.362 (3)	Cr-O-Cr	102.73 (28)
	3.301 (3)		100.75 (27)
	3.254 (3)		105.22 (28)
Cr-O4	2.114 (6)	O-Cr-O	75.45 (25)
			76.59 (25)
Cr-C1	1.778 (14)		73.84 (25)
Cr-C2	1.766 (14)		
Cr-C3	1.776 (13)	Cr-C1-O1	170.4 (12)
		Cr-C2-O2	173.2 (12)
C1-O1	1.186 (18)	Cr-C3-O3	175.4 (11)
C2-O2	1.183 (18)		
C3-O3	1.200 (16)	Cr-O4-C4	116.3 (8)
			116.6 (8)
C4-O4	1.418 (18)		113.3 (8)

[a] Estimated standard deviations in the least significant digits are given in parentheses in this and following tables.

Table III. Atomic Coordinates for $[Et_4N]_4[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]$

atom	*x*	*y*	*z*
Cr	0.03316 (14)	0.07416 (7)	0.15423 (5)
O1	−0.0099 (9)	0.0568 (5)	0.2286 (3)
O2	−0.1954 (9)	0.0579 (5)	0.1564 (3)
O3	0.0293 (8)	−0.0509 (4)	0.1606 (2)
O4	0.0537 (5)	0.0875 (3)	0.1006 (2)
C1	0.0140 (10)	0.0670 (5)	0.1996 (4)
C2	−0.1045 (11)	0.0669 (5)	0.1543 (3)
C3	0.0331 (9)	−0.0006 (5)	0.1567 (3)
C4	−0.0068 (13)	0.0531 (7)	0.0782 (5)
N1	0.1250 (0)	0.1250 (0)	0.5046 (4)
N2	0.1250 (0)	0.1250 (0)	0.3199 (4)
C5	0.117 (2)	0.0724 (9)	0.4820 (6)
C6	0.015 (2)	0.0701 (10)	0.4613 (7)
C7	0.023 (2)	0.131 (2)	0.5221 (8)
C8	0.042 (2)	0.1835 (12)	0.5520 (8)
C9	0.137 (4)	0.180 (2)	0.3446 (11)
C9A	0.205 (5)	0.133 (3)	0.347 (2)
C10	0.235 (2)	0.1812 (12)	0.3630 (8)
C11	0.226 (4)	0.116 (2)	0.2999 (12)
C11A	0.130 (6)	0.178 (2)	0.296 (2)
C12	0.229 (2)	0.0699 (11)	0.2756 (7)

perature factors for the anion Cr, C, and O atoms, isotropic temperature factors for the cation N and C atoms, and bond distances and angles for the Et_4N^+ cation are provided as supplementary material.

A nonbonding Cr–Cr mean distance of 3.31 (6) Å is consistent with a closed-shell configuration for each chromium atom. The average Cr–O–Cr and O–Cr–O bond angles in the Cr_4O_4 core are 102.86 (16) and 75.30 (14)°, respectively. The obtuse Cr–O–Cr and acute O–Cr–O angles, as well as the large metal separation reported here, are very similar to those found in related cubane-like structures of the alternating A_4B_4 type.[16] A few of these compounds (with their average core bond angles and average nonbonding M–M distances) are $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]$[17] (Re–O–Re = 104.0 (5)°, O–Re–O = 74.3 (1)°, Re–Re = 3.480 (2) Å), $[Re_4(CO)_{12}(\mu_3\text{-}SCH_3)_4]$[18] (Re–S–Re = 101.8 (4)°, S–Re–S = 76.8 (3)°, Re–Re = 3.853 (3) Å), $[Mo_4(CO)_8(NO)_4(\mu_3\text{-}OH)_4]$[6] (Mo–O–Mo = 103 (1)°, O–Mo–O = 76 (1)°, Mo–Mo = 3.429 (3) Å), $[W_4(CO)_{12}(\mu_3\text{-}OH)_4H_4]$[7] (W–O–W = 104 (1)°, O–W–O = 74 (1)°, W–W = 3.479 (3) Å). By contrast, a cubane-like Cr(III) cluster, $[(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_4]$, has recently been characterized, but here, short Cr–Cr distances ranging from 2.702 (6) to 2.900 (6) Å and bond angles in the Cr_4O_4 core of 88.8 (1)–96.7 (2)° for Cr–O–Cr and 83.2 (2)–90.1 (1)° for O–Cr–O were found.[19] The acute Cr–O–Cr angles are believed[19] to provide solid evidence for the presence of Cr–Cr single bonds since an approximate tetrahedral angle would result in a nonbonding distance, similar to that found in $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$.

The mean bond distances within the chromium coordination sphere of the tetraanion are well-behaved. The $Cr\text{–}O_{\mu_3}$ distance of 2.114 (6) Å is comparable to the above-mentioned cubane-like complexes,[6,7,17] and a bond length of 1.773 (8) Å for $Cr\text{–}C_{CO}$ is shorter than those reported for other trisubstituted $Cr(CO)_6$ derivatives,[20] consistent with the negative charge on the anion. An average C–O distance of 1.191 (10) Å for the orthogonal carbonyl ligands is in agreement with similar anionic M(0) complexes, such as $[W_4(CO)_{12}(\mu_3\text{-}OH)_4H_4]$ (C–O (average) = 1.20 (5) Å).[7] The low infrared carbonyl stretching frequencies found for $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ support recent molecular orbital calculations that predict extensive π-donation to the terminal carbonyl groups for cubane-like systems containing low-valent metals.[21]

Chemistry of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$. Owing to the ease of its preparation, $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ is a useful precursor for entry into the synthesis of other substituted zerovalent chromium carbonyls. As depicted in Figure 1, protonation of the tetraanion with HCl in CH_3CN at room temperature instantly forms $Cr(CO)_3(CH_3CN)_3$ in 96% isolated yield. The original method[11] for preparation of $Cr(CO)_3(CH_3CN)_3$, a complex whose important feature is the facility by which the nitrile ligands can be replaced by other substrates,[22] involves CO displacement from $Cr(CO)_6$ in refluxing CH_3CN. In that case, the yield is also essentially quantitative; however, our experience indicates that reaction periods are undesirably long. A further disadvantage of that method is that unreacted $Cr(CO)_6$ collects in the reflux condenser due to its high volatility under the reaction conditions.

Another useful derivative, $Cr(CO)_3(NH_3)_3$, can be prepared by direct addition of the tetraanion to concentrated ammonium hydroxide. The two-step process shown in eq 1 and 2, via $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$, is a modification of

$$Cr(CO)_6 \xrightarrow{Me_4NOH,MeOH} [Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-} \quad (1)$$

$$[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-} \xrightarrow{NH_4OH} Cr(CO)_3(NH_3)_3 \quad (2)$$

a procedure reported earlier for the synthesis of $Cr(CO)_3(NH_3)_3$, where it was noted that an uncharacterized orange-colored mixture was obtained under pressure reactor conditions by treatment of $Cr(CO)_6$ with a 7.5-fold molar excess of 95% ethanolic KOH.[10] In a similar experiment using MeOH as solvent, we isolated a highly insoluble orange solid which exhibited an infrared pattern (Nujol mull, ν(CO) 1860 (s), 1695 (vs, br) cm^{-1}) very similar to that of the tetraanion. The extreme insolubility of this salt precluded further spectroscopic investigation, but metathesis with Et_4NBr in CH_3CN gave a solution with spectroscopic properties and a reactivity pattern identical with that of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$. It seems reasonable that these species formed in MeOH and 95% EtOH can thus be formulated as $K_4[Cr_4(CO)_{12}(\mu_3\text{-}OR)_4]$ (MeOH solvent, R = Me; 95% EtOH solvent, R = Et). Two dif-

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ferent types of bridging ligands, namely μ_3-OH and μ_3-OC_2H_5, may well be present in the species formed in 95% EtOH, however infrared mull samples do not indicate the presence of a bridging hydroxide ligand.[23]

A few mechanistic comments can be made regarding the synthesis of $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ from $Cr(CO)_6$. Little effect on product yield was observed when the hydroxide ion concentration was varied in the range 2.5–5.0 mol of OH^- per mol of $Cr(CO)_6$. Infrared analysis of the reaction solution revealed the presence of $[(\mu\text{-}H)Cr_2(CO)_{10}]^-$.[24] Indeed, $[Cr_4(CO)_{12}(\mu_3\text{-}OCH_3)_4]^{4-}$ can be directly prepared from a methanolic alkaline solution containing only the bridging hydride.

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Registry No. 1, 81097-71-4; 2, 88729-66-2; $Cr(CO)_3(NH_3)_3$, 14974-11-9; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $[Et_4N][Cr(CO)_5Br]$, 14780-93-9.

Supplementary Material Available: Tables of anisotropic and isotropic temperature factors for all atoms, tables of bond lengths and angles for the cations, figures of the ordered cation and disordered cation in each conformation, and structure factor tables (9 pages). Ordering information is given on any current masthead page.

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A Study of σ and π Bonding in Iron Tetracarbonyl Complexes

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Core electron binding energies have been measured for a series of monosubstituted iron carbonyls of the formula $Fe(CO)_4L$, where L = pyridine, trimethylphosphine, acrolein, methyl acrylate, dimethyl maleate, 1,1-dichloroethylene, and *trans*-1,2-dichloroethylene. The core binding energies have been used in conjunction with available valence orbital ionization potentials to compare the bonding properties of the ligands L with carbon monoxide. The method led to the following conclusions: (1) The Fe $d_{x^2-y^2}$, d_{xy} orbitals of the axially coordinated pyridine and trimethylphosphine complexes do not interact with the axial ligands, whereas the Fe d_{xy}, d_{yz} orbitals in these complexes are destabilized by about 0.3 eV relative to $Fe(CO)_5$ because of the loss of the strongly back-bonding CO ligand. (2) The replacement of CO in the equatorial plane with an olefin having electron-withdrawing substituents causes the Fe $d_{x^2-y^2}$, d_{xy} orbitals to be stabilized by 0.2–0.4 eV relative to $Fe(CO)_5$, whereas the Fe d_{xz}, d_{yz} orbitals are destabilized by about 0.3 eV because of their orthogonality to the olefin π^* orbitals. (3) The olefin π orbitals are stabilized by about 0.6 eV by coordination to the $Fe(CO)_4$ fragment, indicating significant σ interaction.

Introduction

We have previously compared the ligand properties of carbon monoxide and ethylene in a study of the photoelectron spectra of $Fe(CO)_4C_2H_4$ and $Fe(CO)_5$.[1] In that study we used both gas-phase core binding energies from X-ray photoelectron spectroscopy (XPS) and valence ionization potentials from ultraviolet photoelectron spectroscopy (UPS). The XPS data were used to correct the UPS data for changes in charge and relaxation energy so that the nature and extent of the molecular orbital interactions accompanying complex formation could be determined unambiguously. We now wish to report the extension of this method to a series of iron tetracarbonyl complexes.

The iron tetracarbonyl complexes which we have chosen for this study are well characterized, and their ultraviolet photoelectron spectra have been previously reported.[2–6] The $Fe(CO)_4L$ compounds fall into two basic classes: those in which the ligand L is a strong σ donor, occupying an axial position of the trigonal bipyramid, and those in which L is an olefin, occupying an equatorial position with the C=C bond in the equatorial plane.

Results

The iron $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies of the $Fe(CO)_4L$ compounds determined in this study and of $Fe(CO)_5$ and $Fe(CO)_4C_2H_4$, determined previously,[1] are presented in Table I. The assignment of the spectra is discussed below.

L = Acrolein, Methyl Acrylate, Dimethyl Maleate. The carbon 1s spectra of all three complexes contain a broad peak at 293.5 eV and a well-resolved narrower peak at 290.4 eV. The area ratios of the higher binding energy peak to the lower binding energy peak are acrolein, 5:2; methyl acrylate, 6:2; dimethyl maleate, 8:2. No appreciable

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