Chromium Tricarbonyl Catecholate Derivatives. Structural and Reactivity Studies of "16-Electron" Complexes[1]

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The formally "16-electron" chromium tricarbonyl catecholate derivative containing a hydrogen-bonded catechol (**1**) has been synthesized from the labile ligand displacement reaction of $Cr(CO)_5THF$ with 2 equiv of the monoprotonated tetraethylammonium salt of catechol in tetrahydrofuran. Complex **2**, the catechol-free derivative, has also been obtained by the removal of the free catechol by the addition of NaOMe. Both complexes have been characterized in solution by infrared and ^{13}C NMR spectroscopies and in the solid-state by X-ray crystallography. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 17.532(4)$ Å, $b = 10.541(4)$ Å, $c = 17.356(7)$ Å, $\beta = 95.18(3)°$, $V = 3194(2)$ Å^3, and $d_{calc} = 1.278$ g/cm^3, for $Z = 4$. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.068(8)$ Å, $b = 20.97(2)$ Å, $c = 12.933(9)$ Å, $\beta = 94.58(6)°$, $V = 2722(4)$ Å^3, and $d_{calc} = 1.233$ g/cm^3, for $Z = 4$, from CH_3CN/toluene/THF. The coordination geometry of the dianion in each case is intermediate between square pyramidal and trigonal bipyramidal, with average Cr–O bond lengths of 2.021[3] and 1.998[9] Å, respectively. Hence, the electronic unsaturation of the chromium center is mitigated in part by π-donation from the catecholate. This phenomenon is enhanced in the absence of intermolecular hydrogen bonding. Evidence for an increase in the π-donating ability of the catecholate ligand when it is not involved in hydrogen-bonding with an added proton donor, such as catechol or methanol, is noted in solution by infrared and ^{13}C NMR spectroscopies. That is, in this instance the ν(CO) vibrations occur at lower frequences and the ^{13}C CO resonances are shifted downfield. Both complexes **1** and **2** are unreactive toward good donor ligands such as PMe_3; however, they react to varying extents with $P(OMe)_3$ and CO, with complex **1** being more reactive.

Introduction

It has long been recognized that metal carbonyl derivatives containing ancillary ligands which have at least one π-donor orbital possess labile carbonyl groups, as a result of enhanced bonding interactions of these ligands with the metal center in the five-coordinate intermediate.[2] For example, $W(CO)_5OPh^-$ readily loses CO ligands and aggregates to afford the dimer and tetramer species $W_2(CO)_6(OPh)_3^{3-}$ and $W_4(CO)_{12}(OPh)_4^{4-}$.[3] Indeed, crystalline $[Et_4N][W(CO)_5OPh]$ is only obtained in the presence of a carbon monoxide atmosphere.[4] This is further illustrated in Scheme 1 for anionic group 6 derivatives, where a variety of clusters have been identified for R = H, alkyl, or aryl.[5] Similar aggregates have been observed for the group 7 metal derivatives.[6]

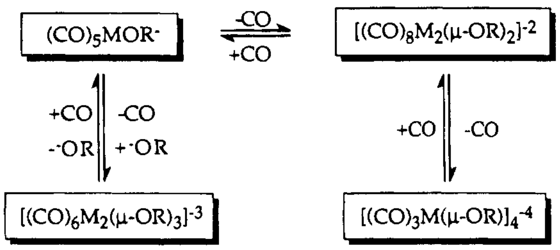
Preliminary rate data from our laboratory indicate that dissociative CO substitution in the anionic carbonyl derivative, $W(CO)_5OPh^-$, by $P(OMe)_3$, eq 1, occurs with a first-order rate

$$W(CO)_5X^- + P(OMe)_3 \rightarrow cis\text{-}W(CO)_4[X]P(OMe)_3^- + CO \quad (1)$$

$$X = OPh^-, Cl^-$$

constant of 2.15×10^{-2} s^{-1} at 5 °C as compared with a value of 1.01×10^{-5} s^{-1} at 5 °C for $W(CO)_5Cl^-$.[7] On the other hand, as might be anticipated,[8] the fluoride analog, $W(CO)_5F^-$, dissociatively loses carbon monoxide at a greatly enhanced rate over the other halide complexes.[7,9] That is, one of the products

Scheme 1



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readily afforded from solutions of $W(CO)_5F^-$ is the dimer $[Et_4N]_3[W_2(CO)_6F_3]$, which was recently crystallographically defined.[10]

Previously, we have reported that the CO ligands in $W(CO)_4(catecholate)^{2-}$ derivatives undergo rapid exchange with ^{13}C-labeled carbon monoxide in solution.[11] Importantly, for the 3,5-di-*tert*-butylcatecholate derivative, the coordinatively unsaturated $[Et_4N]_2[W(CO)_3(catecholate)]$ complex has been isolated and fully characterized by solution NMR/IR spectroscopy and X-ray crystallography. Although the CO ligands are labile in the unsubstituted catecholate tungsten tetracarbonyl derivative, it was not possible to isolate the formally coordinatively unsaturated tricarbonyl species.

As part of our program of studies on the reactivity of metal carbonyls containing ligands capable of π-donation to the metal center, we present herein structural and reactivity investigations of the unsubstituted catecholate ($O_2C_6H_4^{2-}$) derivative of chromium tricarbonyl.

Experimental Section

Methods and Materials. All manipulations were performed on a double-manifold Schlenk line under an atmosphere of argon or in an argon-filled glovebox. Solvents were dried and deoxygenated by distillation from the appropriate reagent under a nitrogen atmosphere. Photolysis experiments were performed using a mercury arc 450-W UV immersion lamp purchased from Ace Glass Co. Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors. Routine infrared spectra were collected using a 0.01-mm CaF_2 cell. ^{13}C NMR spectra were collected on a Varian Unity 500 spectrometer. ^{31}P NMR spectra were collected on a Varian XL-200 spectrometer with a broad-band probe. ^{13}CO was purchased from Cambridge Isotopes and used as received. $Cr(CO)_6$ was purchased from Strem Chemicals Inc. and used without further purification.

Synthesis of $[Et_4N][OC_6H_4OH]$. The synthesis of $[Et_4N][OC_6H_4OH]$ was accomplished by the reaction of HOC_6H_4OH with 1 equiv of Et_4NOH in methanol. The reaction mixture was allowed to stir for 20 min, and the methanol was removed by vacuum overnight, leaving a white solid product.

Synthesis of $[Et_4N]_2[Cr(CO)_3OC_6H_4O]{\cdot}HOC_6H_4OH$ (1). The synthesis of $[Et_4N]_2[Cr(CO)_3OC_6H_4O]{\cdot}HOC_6H_4OH$ was accomplished in yields greater than 90% by the reaction of 2 equiv of $[Et_4N][OC_6H_4OH]$ and $Cr(CO)_5THF$ (prepared by photolysis of 0.30 g of $Cr(CO)_6$ in 30 mL of THF) at ambient temperature. The THF was removed from the reaction mixture by vacuum, leaving behind a bright red powder. The powder was washed several times with hexane to remove any $Cr(CO)_6$ present.

Synthesis of $[Et_4N]_2[Cr(CO)_3O_2C_6H_4O_2C_6H_4]$ (2). The complex $[Et_4N]_2[Cr(CO)_3OC_6H_4O]$ can be prepared by reaction of 1 with a 5-fold excess of sodium methoxide in an acetonitrile solution. The excess sodium methoxide and the produced $Na_2OC_6H_4O$ are easily removed by filtration through Celite. Removal of the solvent by vacuum yields a bright red powder.

Both complexes 1 and 2 are extremely air and moisture sensitive, making carbon/hydrogen elemental analysis difficult. However, the isolated products which were obtained in >90% yields possessed infrared/^{13}C NMR spectral properties identical to those of the crystalline samples which were subjected to X-ray structural analysis.

X-ray Crystallography of 1 and 2. Crystal data and details of data collection are given in Table 1. A bright red block for 1 and red needle for 2 were mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N_2 cold stream. Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (Mo Kα λ = 0.710 73 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 24 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \le 2\theta \le 50.0°$. Three control reflections collected every 97 reflections showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to 5629 reflections for 1 and 5203 reflections for 2. A semiempirical absorption correction was applied. Totals of 2930 unique reflections for 1 and 1552 for 2 with $|I| \ge 2.0\sigma(I)$, were used in further calculations. Both structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1988)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.0668$, $R_w(F^2) = 0.1088$, and $S = 1.02$ at convergence for 1 and $R = 0.0748$, $R_w(F) = 0.0860$, and $S = 1.70$ for 2. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Table 1. Crystallographic Data

	1	**2**
formula	$C_{31}H_{50}N_2O_7Cr$	$C_{25}H_{44}N_2O_5Cr$
formula weight	614.73	504.6
space group	monoclinic, $P2_1/c$	monoclinic $P2_1/n$
a, Å	17.532(4)	10.068(8)
b, Å	10.541(4)	20.97(2)
c, Å	17.356(7)	12.933(9)
β, deg	95.18(3)	94.58(6)
V, Å^3	3194(2)	2722(4)
Z	4	4
d(calc), g/cm^3	1.278	1.233
abs coeff, mm^{-1}	0.405	0.443
λ, Å	0.710 73	0.710 73
T, K	193	193
transm coeff	0.991−0.958	0.8864−0.9853
R,[a] %	6.68	7.48
R_w,[a] %	10.88	8.60[b]
GOF	1.02	1.70

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [b] $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

Results

Synthesis. Complex 1 was prepared in greater than 90% yield by the labile ligand displacement reaction of $Cr(CO)_5THF$ with 2 equiv of the monoprotonated tetraethylammonium salt of catechol in tetrahydrofuran. Complex 1 is completely insoluble in THF, precipitating from solution as a red powder. This reaction presumably proceeds *via* the intermediacy of a pentacarbonyl aryloxide derivative, $Cr(CO)_5OC_6H_4OH^-$, which undergoes deprotonation by free $HOC_6H_4O^-$ with concomitant CO loss and chelation of the catecholate ligand. The synthesis of the catechol-free complex, 2, was achieved by the addition of NaOMe to an acetonitrile solution of 1, which resulted in the precipitation of $Na_2O_2C_6H_4$. The complexes are extremely air-sensitive, decomposing in a few seconds in solution in the presence of oxygen. The general approach to the synthesis of these complexes is outlined in Scheme 2. The infrared spectra of complexes 1 and 2 in the ν(CO) region both in the solid state and in acetonitrile solution are consistent with a $\{Cr(CO)_3\}$ moiety (*vide infra*). Both 1 and 2 are stable in acetonitrile for days under an argon atmosphere, only slowly decomposing at ambient temperature. On the other hand, in pure methanol or in a nitrogen atmosphere decomposition occurs in a few hours.

Structures. Crystals of complex 1 suitable for a single-crystal X-ray structure determination were grown from a concentrated acetonitrile solution, layered with THF and toluene, over a 2-week period at −10 °C. The final atomic positional and equivalent isotropic displacement parameters for complex 1 are listed in Table 2 . Figure 1 shows a drawing of the dianion with hydrogen bonding, and selected bond distances and angles are provided in Table 3. The structure of complex 1 consists

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Scheme 2

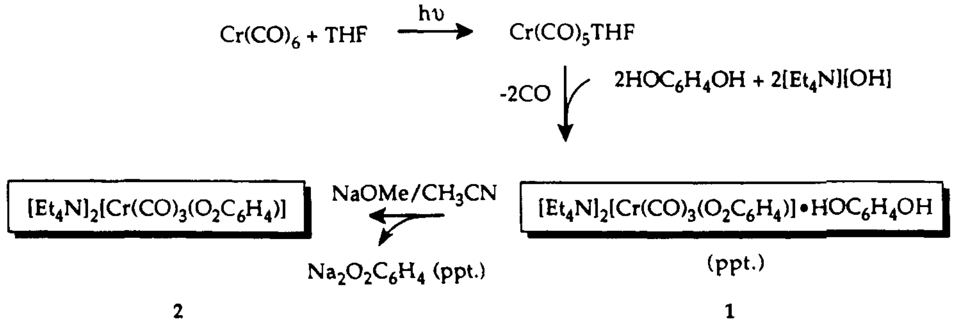

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[Et_4N]_2[Cr(CO)_3C_6H_4O_2]\cdot[C_6H_4O_2H_2]$ (**1**)

	x	*y*	*z*	*U*(eq)[b]
Cr(1)	2198(1)	1760(1)	3180(1)	23(1)
O(1)	914(2)	3648(3)	3002(2)	41(1)
O(2)	1058(2)	220(4)	2199(2)	50(1)
O(3)	1350(2)	871(4)	4483(2)	46(1)
O(4)	3124(2)	607(3)	3152(2)	27(1)
O(5)	3042(2)	3051(3)	3204(2)	23(1)
O(6)	3116(2)	8104(3)	3470(2)	31(1)
O(7)	2958(2)	5534(3)	3513(2)	29(1)
C(1)	1441(3)	2943(4)	3075(3)	27(1)
C(2)	1528(3)	789(5)	2587(3)	29(1)
C(3)	1703(3)	1191(5)	3961(3)	30(1)
C(4)	3792(3)	1221(4)	3123(3)	21(1)
C(5)	3756(3)	2566(4)	3158(3)	20(1)
C(6)	4409(3)	3303(5)	3139(3)	28(1)
C(7)	5116(3)	2692(5)	3082(3)	34(1)
C(8)	5158(3)	1386(5)	3040(3)	34(1)
C(9)	4498(3)	645(5)	3063(3)	29(1)
C(10)	2893(2)	7481(4)	2798(3)	20(1)
C(11)	2803(3)	6146(4)	2823(3)	22(1)
C(12)	2548(3)	5498(4)	2148(3)	25(1)
C(13)	2396(3)	6151(5)	1450(3)	32(1)
C(14)	2504(3)	7451(5)	1425(3)	34(1)
C(15)	2743(3)	8101(5)	2099(3)	29(1)

[a] Estimated standard deviations are given in parentheses. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

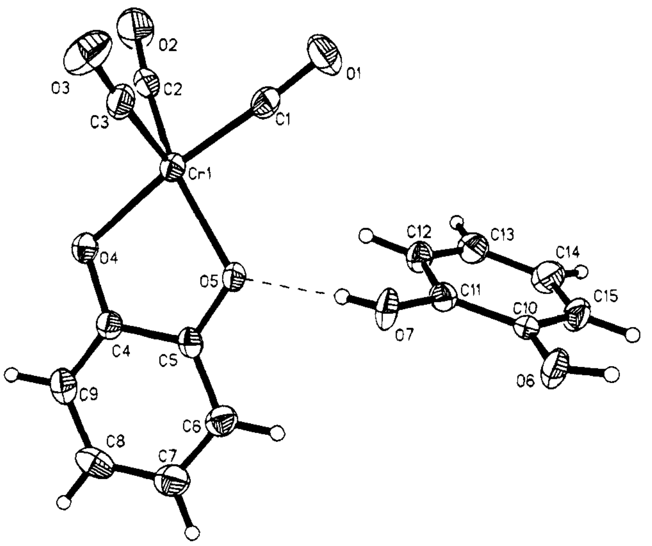

Figure 1. Thermal ellipsoid drawing of the dianion of complex **1** in 50% probability illustrating the intermolecular hydrogen-bonding along with the atomic numbering scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg)[a]

$[Et_4N]_2\,[Cr(CO)_3C_6H_4O_2]\cdot[C_6H_4O_2H_2]$ (**1**)			
Cr(1)-C(3)	1.779(6)	Cr(1)-C(2)	1.807(5)
Cr(1)−C(1)	1.818(5)	Cr(1)−O(5)	2.008(3)
Cr(1)−O(4)	2.033(3)	O(4)−C(4)	1.343(5)
O(5)−C(5)	1.361(5)	O(6)−C(10)	1.366(5)
O(7)−C(11)	1.365(5)	O(7)−O(5)	2.687(11)
C(3)−Cr(1)−C(2)	84.6(2)	C(3)−Cr(1)−C(1)	84.6(2)
C(2)−Cr(1)−C(1)	84.3(2)	C(3)−Cr(1)−O(5)	128.5(2)
C(2)−Cr(1)−O(5)	146.7(2)	C(1)−Cr(1)−O(5)	93.8(2)
C(3)−Cr(1)−O(4)	105.2(2)	C(2)−Cr(1)−O(4)	97.3(2)
C(1)−Cr(1)−O(4)	170.2(2)	O(5)−Cr(1)−O(4)	79.46(12)
C(4)−O(4)−Cr(1)	114.4(3)	C(5)−O(5)−Cr(1)	115.1(3)
$[Et_4N]_2[Cr(CO)_3C_6H_4O_2]$ (**2**)			
Cr(1)−O(4)	1.992(9)	Cr(1)−O(5)	2.003(9)
Cr(1)−C(1)	1.81(1)	Cr(1)−C(2)	1.79(1)
Cr(1)−C(3)	1.78(1)	O(4)−C(4)	1.35(1)
O(5)−C(9)	1.34(1)		
O(4)−Cr(1)−O(5)	80.0(4)	O(4)−Cr(1)−C(1)	119.3(5)
O(5)−Cr(1)−C(1)	111.7(5)	O(4)−Cr(1)−C(2)	156.8(5)
O(5)−Cr(1)−C(2)	94.8(5)	C(1)−Cr(1)−C(2)	83.7(6)
O(4)−Cr(1)−C(3)	92.5(5)	O(5)−Cr(1)−C(3)	162.2(5)
C(1)−Cr(1)−C(3)	86.1(6)	C(2)−Cr(1)−C(3)	85.7(6)
Cr(1)−O(4)−C(4)	113.7(8)	Cr(1)−O(5)−C(9)	114.3(8)
Cr(1)−C(1)−O(1)	178(1)	Cr(1)−C(2)−O(2)	176(1)
Cr(1)−C(3)−O(3)	177(1)		

[a] Estimated standard deviations are given in parentheses.

of a $Cr(CO)_3$ residue chelated by a doubly deprotonated catechol. Each oxygen of the chelating catecholate is hydrogen-bound to a free catechol, forming a continuous linear chain of molecules, completely correspondent to our previously presented $[Et_4N]_2$-$[W(CO)_4O_2C_6H_4]\cdot HOC_6H_4OH$ structure.[11] The charge on the chromium center is balanced by two tetraethylammonium cations. The O···O distance is 2.687 Å, which is slightly longer than that reported for the tungsten *tetra*carbonyl analog, where the O···O distance is 2.535 Å, and shorter than the reported value of 2.796 Å for crystalline catechol.[12] Similar O···O distances in low-valent metal phenoxide derivatives hydrogen-bonded to alcohols or water have been noted.[4,13] The average Cr−C bond length of the carbonyls is 1.801[9] Å which is comparable to previously reported values for a 16-electron chromium center.[14,15] The Cr-O bond distances were determined to be 2.033(3) and 2.008(3) Å. The C−O bond lengths of the chelated catecholate moiety are 1.343(5) and 1.361(5) Å, and the C−O bond lengths of the hydrogen-bound catechol are 1.365(5) and 1.366(5) Å; the former parameters are well within the expected range for a catecholate as compared to those normal

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Et_4N]_2[Cr(CO)_3C_6H_4O_2]$ (**2**)[a]

	x	*y*	*z*	*U*(eq)[b]
Cr(1)	2214(2)	2242(1)	4416(2)	29(1)
O(1)	1516(10)	1629(4)	2365(7)	52(4)
O(2)	393(9)	1229(4)	5123(7)	50(4)
O(3)	4290(10)	1229(4)	4738(7)	52(4)
O(4)	3551(9)	2943(4)	4542(6)	39(4)
O(5)	1021(9)	2979(4)	4675(6)	36(3)
C(1)	1791(13)	1883(6)	3163(10)	31(5)
C(2)	1107(13)	1652(6)	4857(9)	32(5)
C(3)	3468(14)	1641(6)	4588(10)	36(5)
C(4)	3029(14)	3514(6)	4756(9)	30(5)
C(5)	3799(13)	4067(6)	4954(9)	35(5)
C(6)	3170(17)	4643(6)	5235(10)	44(6)
C(7)	1837(17)	4655(6)	5327(10)	44(6)
C(8)	1059(13)	4110(6)	5111(9)	36(5)
C(9)	1662(13)	3535(7)	4851(9)	31(5)

[a] Estimated standard deviations are given in parentheses. [b] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

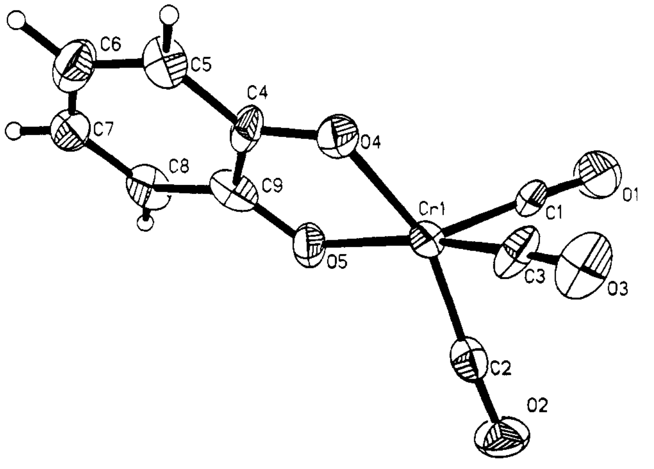

Figure 2. Thermal ellipsoid drawing of the dianion of complex **2** in 50% probability with the atomic numbering scheme.

for a quinone or semiquinone. C—O bond lengths in catecholate compounds have generally been found to be around 1.35(1) Å, while the bond distances in semiquinone and quinone species are near 1.29(1) and 1.23(1) Å respectively.[16] The coordination about the Cr metal center is intermediate between that of a distorted square pyramid and trigonal bipyramid geometry with the chromium atom, the two oxygens of the catechol and two of the carbonyls forming the base of the pyramid and the third carbonyl forming the apex. The O(4)—Cr—O(5) bite angle is 79.46(12)°, slightly larger than that of the tungsten analog where the angle is 75.5(4)°. A least-squares plane through the base of the pyramid shows a mean deviation of 0.21 Å from planarity, and the carbonyl carbon of the apex is 1.89 Å away from the plane.

Crystals of complex **2** suitable for X-ray crystal studies were obtained from a concentrated solution of acetonitrile, layered with toluene and THF, after a period of 1 month at −10 °C. The final atomic positional and equivalent isotropic displacement parameters are given in Table 4. Figure 2 shows a drawing of the dianion, and selected bond distances and angles are given in Table 3. The structure of **2** is analogous to that of **1** with the exception of the hydrogen-bound catechol. Two tetraethylammonium cations are present to balance the charge. The average Cr—C bond distance of the carbonyls is 1.79[2] Å and the Cr—O distances are 1.992(9) and 2.003(9) Å. The C—O bond lengths of the catecholate ligand are 1.34(2) and 1.35(1) Å, again in the proper range for a catecholate. A least-squares plane through the chromium atom, the two oxygens of the catechol, and two of the carbonyls yields a mean deviation from planarity of 0.11, Å with the third carbonyl carbon sitting 1.94 Å away from this plane. The bite angle of the chelating catechol is 80.0(4)°, nearly the same as that for the hydrogen-bound species.

Spectral Properties. Complex **1** exhibits two strong infrared bands in the ν(CO) region in acetonitrile solution at 1879 and 1742 cm^{-1} of the expected intensity pattern for a metal tricarbonyl species with approximately C_{3v} local symmetry.[17] Similar ν(CO) bands are observed in the solid state (KBr) with frequencies of 1873 and 1734 cm^{-1}. Complex **2** exhibited two ν(CO) infrared vibrations at 1874 and 1735 cm^{-1} in acetonitrile of the same intensity pattern as that noted for **1**. This shift to slightly lower wavenumbers is consistent with an increase in electron density at the metal center due to the absence of the electron-withdrawing properties of hydrogen bonding by the catechol. The solid-state KBr infrared spectrum of **2** in the ν(CO) region showed a change from C_{3v} symmetry as revealed by a splitting of the, lower frequency, E band into two distinct bands at 1737 and 1705 cm^{-1}, with the A mode appearing at 1869 cm^{-1}.

The effects of the hydrogen-bonded catechol can also be seen in the ^{13}C NMR spectrum of **1**. That is, at −40 °C complex **1** exhibits a single, sharp signal for the carbonyl carbons at 245.0 ppm in CH_3CN, whereas complex **2** shows one resonance at 248.0 ppm at ambient temperature. This latter ^{13}C resonance displayed no shifting or broadening upon cooling of the sample to −35 °C, indicative of a fast intramolecular equilibration of the three magnetically inequivalent CO ligands even at low temperature. In the case of the analogous tungsten derivative, $[W(CO)_3(O_2C_6H_4)]^{2-}$, a broadening of the ^{13}C signal for the three carbonyl ligands was noted in acetonitrile at −35 °C, suggestive of a somewhat slower scrambling process in this instance.[11] The downfield shift of 3 ppm in the ^{13}C resonance for the CO ligands in **2** as compared to **1** is compatible with an increase in the electron donor property of the catecholate ligand in the absence of intermolecular hydrogen bonding. On the other hand, the hydrogen-bonded species, **1**, is in equilibrium with the non-hydrogen-bonded complex in acetonitrile. The coalescence temperature for the intermolecular process described in eq 2 is close to 20 °C, where no ^{13}C signal is observed for

$$\underset{\mathbf{1}\ (245\ \text{ppm})}{[Cr(CO)_3(O_2C_6H_4)]{\cdot}HOC_6H_4OH^{2-}} \rightleftharpoons \underset{\mathbf{2}\ (248\ \text{ppm})}{[Cr(CO)_3(O_2C_6H_4)]^{2-}} + HOC_6H_4OH \quad (2)$$

the carbonyl ligands (*vide infra*). The rate constant for the equilibration between these two species (**1** and **2**) at 20 °C is estimated to be around $8.3 \times 10^2\ s^{-1}$. Table 5 lists a summary of infrared and NMR data for these complexes.

Hydrogen-bonding effects become more apparent upon dissolving complex **2** in methanol. The infrared spectrum in methanol in the ν(CO) region exhibits a large shift to higher frequencies and a splitting in the E band, from 1874 and 1735 cm^{-1} in CH_3CN to 1895, 1767, and 1733 cm^{-1}. The effects of added methanol can also be seen in acetonitrile solution. Addition of 0.5 mL of MeOH to 10 mL of a 0.020 M acetonitrile solution of complex **2** produces a shift in the infrared spectrum

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(16) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(17) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; p 44.

Table 5. Infrared Stretching Frequencies and ^{13}C NMR Data for **1** and **2**

	1	**2**
ν(C≡O), cm^{-1} (CH$_3$CN)	1879 (s), 1742 (vs)	1874(s), 1735 (vs)
ν(C≡O), cm^{-1} (KBr)	1873 (s), 1734 (vs)	1869 (s), 1737 (s), 1705 (s)
ν(C≡O), cm^{-1} (MeOH)		1895 (s), 1767 (s), 1733 (s)
δ(^{13}C≡O), ppm[a]	245[b]	248[c]

[a] Spectra determined in acetonitrile-d_3. [b] Spectrum measured at −40 °C. [c] Spectrum measured at −35 °C.

to higher wavenumbers, to 1883 and 1739 cm^{-1}. This shift is increased by adding another 0.5 mL of MeOH; this time the bands appear at 1885 and 1744 cm^{-1}. Addition of a total of 1.5 mL or more of MeOH results in the ν(CO) bands remaining constant at 1886 and 1747 cm^{-1} with the band at 1747 cm^{-1} exhibiting some broadening.

Similar to that noted for the catechol hydrogen-bonded complex **1** in acetonitrile, the ^{13}C NMR resonance for the CO ligands of **2** in CH$_3$CN in the presence of excess methanol appears as a broad signal centered at 246.0 ppm at ambient temperature. Upon lowering of the temperature to −35 °C, the CO resonance becomes sharp and shifts upfield slightly to 245.2 ppm, indicative of a quenching of **2** as its methanol hydrogen-bonded adduct at this temperature. As a consequence of employing the more weakly hydrogen-bonding reagent CD$_3$OD, the coalescence temperature is lowered as indicated by the absence of a ^{13}C signal for the CO ligands in **2** at ambient temperature in CH$_3$CN in the presence of excess deuterated methanol. Figure 3 summarizes the behavior of the ^{13}C resonance for the carbonyl ligands in complex **2** in the presence of excess methanol.

Complexes **1** and **2** are unreactive toward PPh$_3$ or PMe$_3$; however, both react with P(OMe)$_3$ in acetonitrile to provide the phosphite adduct as revealed by ^{31}P NMR spectroscopy (eq 3).

$$\mathrm{Cr(CO)_3(O_2C_6H_4)^{2-} + P(OMe)_3 \rightleftharpoons Cr(CO)_3(O_2C_6H_4)P(OMe)_3^{2-}} \quad (3)$$

The extent of reaction of the [Cr(CO)$_3$(O$_2$C$_6$H$_4$)]$^{2-}$ anion with P(OMe)$_3$ is highly dependent on whether the oxygen lone pairs of the catecholate ligand are involved in intermolecular hydrogen-bonding. For example, at ambient temperature, the ^{31}P NMR spectrum of an acetonitrile solution of complex **1** in the presence of 1 equiv of P(OMe)$_3$ exhibits two peaks, an intense signal at 183 ppm for a metal-bound P(OMe)$_3$ ligand and a much less intense resonance at 141 ppm due to free phosphite.[18-20] Upon lowering of the temperature to −30 °C, the ^{31}P resonance at 183 ppm due to the P(OMe)$_3$ adduct increases in intensity with concomitant appearance of a ^{31}P signal at 179 ppm. This latter peak is due to P(OMe)$_3$ interacting with the non-hydrogen-bonded complex, **2** (*vide infra*). When the temperature is raised to 20 °C, the signal at 179 ppm disappears, with a simultaneous returning of the 183 ppm signal to its original intensity prior to the lowering of the temperature.

In the absence of catechol for intermolecular hydrogen-bonding with the metal-bound catecholate, [Cr(CO)$_3$(O$_2$C$_6$H$_4$)]$^{2-}$ is unreactive toward 1 equiv of P(OMe)$_3$. That is, the ^{31}P NMR spectrum in this instance exhibits a single resonance at 141 ppm due to free P(OMe)$_3$. However, when the temperature is lowered to −35 °C, an additional ^{31}P signal is noted at 179 ppm which is assigned to the metal−phosphite adduct. This ^{31}P signal constitutes 6% of the intensity of the free phosphite resonance. When the temperature is increased in increments of 5 °C, the resonance at 179 ppm slowly decreases in intensity until it has nearly disappeared at 0 °C with a concomitant increase in the intensity of the 141 ppm signal. As anticipated, the interaction of complex **2** with P(OMe)$_3$ is greatly enhanced in the presence of added methanol. When about 3 equiv of MeOH is added to an acetonitrile solution of **2** containing 1 equiv of P(OMe)$_3$, the ^{31}P signal for bound P(OMe)$_3$ occurs at 182 ppm. At ambient temperature, the ratio of bound to free P(OMe)$_3$ is nearly 1. When the temperature is lowered to −35 °C, the resonance at 141 ppm for the free phosphite decreases greatly, with a concomitant increase in the 182 ppm signal. Warming the solution in increments of 5 °C leads to an increase in the 141 ppm resonance with a simultaneous decrease in the ^{31}P signal at 182 ppm, until the original spectrum is again observed at 20 °C. Using larger quantities of MeOH, about 10% by volume, results in only a small amount of unbound P(OMe)$_3$ ligand being observed by ^{31}P NMR. Furthermore, there was no change in the intensity ratio of bound to unbound P(OMe)$_3$ over the temperature range of −30 to +25 °C. However, warming the solution to 40 °C led to substantial decomposition of the complex.

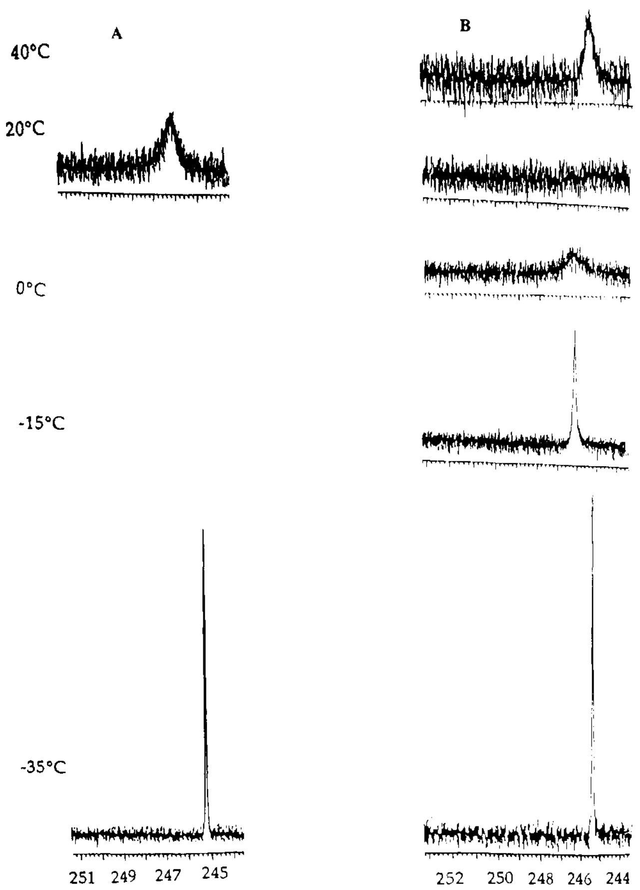

Figure 3. Temperature dependence of the ^{13}C NMR spectrum of the CO ligands in complex **2**: (A) in acetonitrile with added CH$_3$OH; (B) in acetonitrile with added CD$_3$OD.

In a similar manner, the catechol or methanol adducts of [Cr(CO)$_3$(O$_2$C$_6$H$_4$)]$^{2-}$ react to a small extent (<20%) with free carbon monoxide in acetonitrile at −35 °C to afford the intermolecularly hydrogen-bonded tetracarbonyl derivatives. The catechol adducts displayed two ^{13}C NMR CO resonances of

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(18) Wang, N.-F.; Wink, D. J.; Dewan, J. C. *Organometallics* **1990**, *9*, 335.

(19) The ^{31}P resonance for free P(OMe)$_3$ has been reported at 141 ppm.[20]

(20) Sohár, P. *CRC Handbook*; CRC Press, Inc.: Boca Raton, FL, 1984; Vol. 2, p 268.

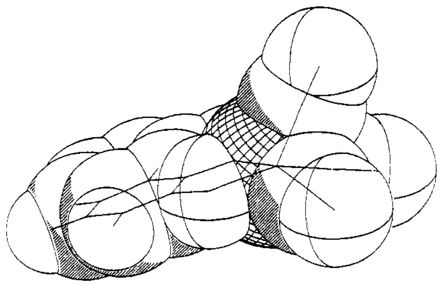

Figure 4. Space-filling model of the dianion of complex **2**.

equal intensity at 229.0 and 212.6 ppm, with the corresponding methanol adduct's ^{13}C signals occurring at 230.0 and 213.6 ppm. When solutions of the tetracarbonyl adducts are warmed to ambient temperature, decomposition of the catecholate complex occurred with formation of $Cr(CO)_{6-n}(CH_3CN)_n$ (n = 0–3) derivatives.

Discussion

It is quite clear from these studies that the *tricarbonyl* catecholate complex of chromium, formally a 16-electron dianion, is thermodynamically stable with respect to the addition of a donor ligand. That is, reaction 4 occurs only reluctantly

$$Cr(CO)_3(O_2C_6H_4)^{2-} + L \rightleftharpoons Cr(CO)_3(O_2C_6H_4)L^{2-} \quad (4)$$

for L = good π-acceptor ligands, such as CO or $P(OMe)_3$, and in the presence of intermolecular hydrogen-bonding reagents which decrease the π-donating ability of the catecholate ligand. Furthermore, as the space-filling model of complex **2** indicates, there are no steric contraints to formation of a hexacoordinate complex (Figure 4). This observation is in sharp contrast with that noted for the tungsten derivatives, where, even when a catecholate ligand with electron-releasing substituents is employed, the tetracarbonyl species has been fully characterized.[11,21] That is, reaction 4 readily takes place at ambient temperature when the metal is tungsten. This is evidently due to a better matching of the chromium acceptor orbitals with the corresponding π-donor orbitals of the catecholate ligand. These observations are in complete agreement with those previously reported upon involving $[Mn(CO)_3(DBCat)]^-$ (DBCat = 3,5-di-*tert*-butylcatecholate), which is essentially isostructural with $Cr(CO)_3(O_2C_6H_4)^{2-}$.[22] In this instance, similar conclusions with regard to the importance of the π-donating ability of catecholates were presented, including comparisons for Mn and Re analogous to those put forth herein for Cr and W. On the other hand, the dithiolate tricarbonyl complexes of chromium readily react with CO to afford the coordinatively and electronically saturated tetracarbonyl derivatives (eq 5).[14]

$$Cr(CO)_3(S_2C_6R_4)^{2-} + CO \rightleftharpoons Cr(CO)_4(S_2C_6R_4)^{2-} \quad (5)$$

$$R = Cl, Me$$

The environment about the chromium center in the complexes reported upon herein is five-coordinate, with three CO ligands and two oxygen donors in a coordination geometry intermediate between trigonal bipyramidal and square pyramidal. For example, in complex **2**, as indicated in Figures 2 and 4, the plane defined by the two oxygen atoms (O(4) and O(5)) and the two carbons (C(2) and C(3)) of the CO ligands has a mean deviation of 0.0469 Å, with the chromium atom being 0.331 Å out of the plane toward the third CO ligand. Although the structure of the tetracarbonylchromium complex is unavailable for comparison with **2**, in the case of the tungsten analogs it is clear that there are structural changes additional to simple removal of the CO ligand from the tetracarbonyl complex upon formation of the tricarbonyl species (see supporting information).

A ball-and-stick representation of complex **1** which contains a summary of the *intraligand* bond distances in the bound catecholate ligand and the catechol which is involved in hydrogen-bonding interaction with the catecholate's oxygen atom is contained in the supporting information. As is readily observable, all comparable bond distances between the catecholate and catechol moieties are quite similar, including the C–O bond lengths. This clearly indicates that the ligand is in the catecholato and not *o*-quinonoid form.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE91-19737) is greatly appreciated.

Supporting Information Available: Tables of anisotropic thermal parameters, bond lengths, and bond angles for complexes **1** and **2**, ORTEP drawings of complexes **1** and **2** showing both cations present, an overlay of stick drawings of (3,5-di-*tert*-butylcatecholate)$W(CO)_4^{2-}$ and (3,5-di-*tert*-butylcatecholate)$W(CO)_3^{2-}$ taken from refs 11 and 21, and a ball-and-stick drawing of **1** indicating intramolecular bond distances in the catecholate and catechol units (10 pages). Ordering information is given on any current masthead pages.

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[21] Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. Submitted for publication.

[22] (a) Hartl, F.; Stufkens, D. J.; Vlček, A., Jr. *Inorg. Chem.* **1992**, *31*, 1687. (b) Hartl, F.; Vlček, A., Jr.; deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 1073.