

# Coordinatively Unsaturated Derivatives of Group 6 Metal Carbonyls Containing the $\pi$ -Donating Ligand 3,5-Di-*tert*-butylcatecholate

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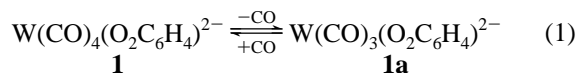
Received July 28, 1995<sup>⊗</sup>

The series of group 6 metal tricarbonyl derivatives of di-*tert*-butylcatecholate have been synthesized from the reactions of  $M(\text{CO})_5\text{THF}$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) with 2 equiv of  $[\text{Et}_4\text{N}][3,5\text{-}^t\text{Bu}_2\text{OC}_6\text{H}_2\text{OH}]$ . Subsequent removal of the free catechol was achieved by the addition of NaOMe. The complexes were shown by X-ray crystallography to exhibit coordinatively unsaturated  $M^\circ$  centers. These metal dianions which have formally  $16e^-$  configurations are stabilized by  $\pi$ -donation from the oxygen atoms of the catecholate ligand. This is evident from the short  $M\text{--O}$  bond distances, e.g., for  $M = \text{W}$ , 2.059(6) Å vs 2.151(4) Å for a single bond. The structures of these five-coordinate dianions can be loosely defined as trigonal bipyramidal with the more electron-rich oxygen donor of the catecholate (ortho to the electron-releasing *tert*-butyl substituent) occupying an equatorial site as indicated by a shorter  $M\text{--O}$  bond length. The tungsten derivative was shown to reversibly react with CO or phosphines to afford the  $18e^-$ , saturated complexes. Although the molybdenum tricarbonyl derivative reacts with CO to partially provide the tetracarbonyl complex, the analogous process involving chromium did not occur. That is, the formation of an  $\text{O}\rightarrow\text{M}$   $\pi$  bond vs an additional  $M\text{--CO}$  bond is favored for  $M = \text{chromium}$ . Complex 2,  $[\text{Et}_4\text{N}]_2[\text{W}(\text{CO})_4\text{DTBCat}]$ , crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 10.013(5)$  Å,  $b = 43.921(14)$  Å,  $c = 9.113(4)$  Å,  $\beta = 115.76(3)^\circ$ ,  $V = 3609(3)$  Å<sup>3</sup>, and  $d_{\text{calc}} = 1.429$  g/cm<sup>3</sup>, for  $Z = 4$ . Complex 4,  $[\text{Et}_4\text{N}]_2[\text{Mo}(\text{CO})_3\text{DTBCat}]$ , crystallized in the monoclinic space group  $C2$  with  $a = 18.255(7)$  Å,  $b = 8.596(3)$  Å,  $c = 22.369(7)$  Å,  $\beta = 91.05(6)^\circ$ ,  $V = 3510(2)$  Å<sup>3</sup>, and  $d_{\text{calc}} = 1.251$  g/cm<sup>3</sup>, for  $Z = 4$ . Similarly, complex 5,  $[\text{Et}_4\text{N}]_2[\text{Cr}(\text{CO})_3\text{DTBCat}]$ , crystallized in the monoclinic space group  $C2$  with  $a = 18.09(2)$  Å,  $b = 8.553(3)$  Å,  $c = 21.927(11)$  Å,  $\beta = 91.09(8)^\circ$ ,  $V = 3393(4)$  Å<sup>3</sup>, and  $d_{\text{calc}} = 1.208$  g/cm<sup>3</sup>, for  $Z = 4$ .

## Introduction

It is well-established that  $\pi$ -donation from an ancillary ligand in a metal complex can stabilize the coordinatively unsaturated intermediate afforded concomitantly with ligand substitution reactions (Scheme 1), thereby enhancing the rate of ligand substitution processes.<sup>1</sup> If  $L = \text{carbon monoxide}$ , in the vernacular of Brown and co-workers,<sup>2</sup>  $A$  is referred to as a *CO-labilizing* ligand. In recent years it has become apparent that, in several instances,  $\pi$ -donating in the  $A\rightarrow M$  bond is favored or nearly thermodynamically neutral with formation of an addition  $M\text{--}L'$  bond. Hence, the coordinatively and electronically unsaturated species resulting from  $L$  dissociation are isolable and subject to thorough characterization.<sup>3–8</sup>

Relevant to this theme, we have previously communicated that the tungsten(0) catecholate complex  $[\text{Et}_4\text{N}]_2[\text{W}(\text{CO})_4(\text{O}_2\text{C}_6\text{H}_4)]$  undergoes facile CO dissociation in acetonitrile solution to afford the coordinatively unsaturated tricarbonyl derivative (eq 1).<sup>9</sup> Complex 1 was structurally characterized

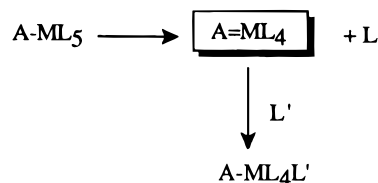


as its hydrogen-bonded derivative with catechol, where the structure displayed strong hydrogen-bonding interactions ( $\text{O}\cdots\text{O} = 2.535(10)$  Å) typical of those seen in a variety of low-valent metal, alkoxides or aryloxides.<sup>10</sup> The tricarbonyl derivative (**1a**)

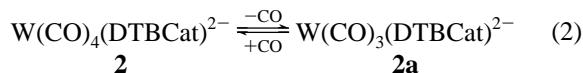
<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, February 15, 1996.

- (1) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley and Sons: New York, 1967.  
 (2) (a) Brown, T. L.; Atwood, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 3160.  
 (b) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.

## Scheme 1

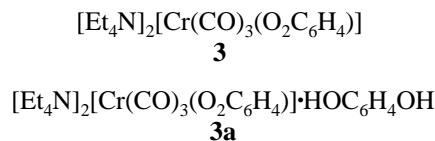


was characterized in solution by means of  $\nu(\text{CO})$  and <sup>13</sup>C NMR spectroscopies. Hence, it was not possible to ascertain whether a solvent molecule ( $\text{CH}_3\text{CN}$ ) was also in the metal coordination sphere. However, upon utilization of the more electron-rich di-*tert*-butyl-substituted catecholate, the tricarbonyl dianion was isolated and crystallized, allowing for a definitive structural analysis by X-ray crystallography (eq 2). Indeed, complex **2a**



was shown to be the coordinatively unsaturated species. As noted in eqs 1 and 2, both processes are reversible.

By way of contrast, the similarly synthesized chromium unsubstituted catecholate derivative,  $[\text{Et}_4\text{N}]_2[\text{Cr}(\text{CO})_3(\text{O}_2\text{C}_6\text{H}_4)]$ , exists exclusively as the tricarbonyl complex.<sup>11</sup> This formally “16-electron” complex has been structurally defined both with and without a hydrogen-bonded catechol, complexes **3** and **3a**.



In an effort to systematically examine both the structural and reaction chemistry of these very interesting coordinatively-unsaturated complexes, we have prepared the molybdenum and chromium analogs of **2a**, complexes **4** and **5**, and have obtained crystals suitable for single-crystal X-ray structure determinations. This has allowed for a comparison of the chemistry of a family (group 6) of metal complexes. In addition, complex **2** was isolated and structurally characterized in order to correlate the geometries of tetracarbonyl and tricarbonyl anions of tungsten. It is important to note at this point that the isoelectronic manganese monoanion analog of complex **5** has been previously thoroughly examined by Vlček and co-workers.<sup>5,6</sup>

## 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 at room temperature unless otherwise noted. 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. Solution infrared spectra were collected using a 0.01-mm CaF<sub>2</sub> cell. Carbon-13 NMR spectra were collected on either a Varian XL-200 spectrometer or a Varian XL-500 spectrometer. <sup>31</sup>P NMR spectra were collected on a Varian XL-200 spectrometer equipped with a broad-band probe. <sup>13</sup>CO was purchased from Cambridge Isotope and used as received. Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and W(CO)<sub>6</sub> were purchased from Strem Chemicals Inc. and used without further purification.

**Synthesis of [Et<sub>4</sub>N][DTBCatH].** The synthesis of [Et<sub>4</sub>N][DTBCatH] was accomplished by the reaction of DTBCatH<sub>2</sub> with 1 equiv of Et<sub>4</sub>NOH in methanol in a 100 mL Schlenk flask. The reaction mixture was allowed to stir for 20 min, and the methanol was removed by vacuum, leaving behind a light violet solid product. Due to the light-sensitive nature of this material, efforts were made to exclude light from the reaction flask.

**Synthesis of [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat]·[DTBCatH<sub>2</sub>].** The synthesis of [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat]·[DTBCatH<sub>2</sub>] (M = group 6 metal) was accomplished in yields greater than 90% by the reaction of 2 equiv of [Et<sub>4</sub>N][DTBCatH] and M(CO)<sub>5</sub>THF (prepared by photolysis of M(CO)<sub>6</sub> in 60 mL of THF; for M = W 0.5 g, for M = Mo 0.4 g, and for M = Cr 0.3 g were used) at ambient temperature. The THF was removed from the reaction mixture *via* cannula, leaving behind an orange powder for M = W, a yellow-orange powder for M = Mo, and a bright red powder for M = Cr. The powders were washed several times with hexane to remove any M(CO)<sub>6</sub> present.

**Synthesis of [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat].** The complex [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat] (M = group 6 metal) can be prepared by reaction of [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat]·[DTBCatH<sub>2</sub>] with a 5-fold excess of sodium methoxide in an acetonitrile solution. The excess sodium

**Table 1.** Crystallographic Data for Complexes **2**, **4**, and **5**

	<b>2</b>	<b>4</b>	<b>5</b>
formula	C <sub>34</sub> H <sub>60</sub> N <sub>2</sub> O <sub>6</sub> W	C <sub>33</sub> H <sub>60</sub> N <sub>2</sub> O <sub>5</sub> Mo	C <sub>33</sub> H <sub>60</sub> N <sub>2</sub> O <sub>5</sub> Cr
fw	776.7	660.77	616.83
space group	monoclinic, P2 <sub>1</sub> /c	monoclinic, C2	monoclinic, C2
a, Å	10.013(5)	18.255(7)	18.09(2)
b, Å	43.921(14)	8.596(3)	8.553(3)
c, Å	9.113(4)	22.369(7)	21.927(11)
β, deg	115.76(3)	91.05(6)	91.09(8)
V, Å <sup>3</sup>	3609(3)	3510(2)	3393(4)
Z	4	4	4
d <sub>calc</sub> , g/cm <sup>3</sup>	1.429	1.251	1.208
abs coeff, mm <sup>-1</sup>	3.309	0.412	0.377
λ, Å	0.710 73	0.710 73	0.710 73
T, K	193	193	163
transm coeff	0.5348–0.9955	0.8408–0.9054	
R <sup>a</sup> %	4.6	7.19	8.00
R <sub>w</sub> <sup>a</sup> %	4.9 <sup>b</sup>	15.89	17.05
GOF	2.21	1.035	1.104

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

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

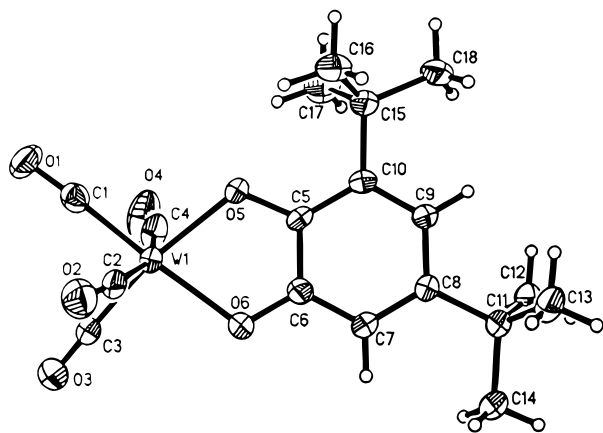
methoxide and the produced Na<sub>2</sub>DTBCat are easily removed by filtration through Celite. Removal of the solvent by vacuum provided a powder. For M = W, a tricarbonyl (**2a**) and a tetracarbonyl (**2**) are observed. For M = Mo, only a tricarbonyl (**4**) and, for M = Cr, only a tricarbonyl (**5**) are observed on the basis of infrared spectra in the ν(CO) region.

**X-ray Crystallography of **2**, **4**, and **5**.** Crystal data and details of data collection are given in Table 1. A bright orange block for **2**, a yellow block for **4**, and a bright red needle for **5** were mounted on a glass fiber with epoxy cement at room temperature. **2** and **4** were cooled to 193 K, and **5** was cooled to 163 K in a N<sub>2</sub> cold stream. Preliminary examination and data collection were performed on a Nicolet R3m/v X-ray diffractometer for **2** and **4** and a Rigaku AFC5 X-ray diffractometer for **5** (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° ≤ 2θ ≤ 50.0°. For **2**, the scintillation aperture was minimized to decrease overlap of adjacent reflections. Three control reflections collected every 97 reflections for **2** and **4** and every 150 reflections for **5** 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 6844 reflections for **2**, 3401 for **4**, and 3242 for **5**. A semiempirical absorption correction was applied for **2** and **4**. DIFABS was applied to correct for absorption for **5**. A total of 6326 unique reflections for **2**, 3301 for **4**, and 3189 for **5** with |I| ≥ 2.0σ<sub>I</sub> were used in further calculations. Structures **2** and **4** were solved by direct methods, and structure **5** was solved by Patterson synthesis [SHELXS, SHELXTL-PLUS program package, Sheldrick (1988, 1993)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R = 0.046, R<sub>w</sub>(F) = 0.049, and S = 2.21 at convergence for **2**, R = 0.0719, R<sub>w</sub>(F<sup>2</sup>) = 0.1589, and S = 1.035 for **4**, and R = 0.0800, R<sub>w</sub>(F<sup>2</sup>) = 0.1705, and S = 1.104 for **5**. Two of the three carbonyl ligands of complex **4** were found to be disordered over two sites. The sites were allowed to be partially occupied, and their site occupation factors were refined (0.49 C(2), O(2), C(3), O(3); 0.51 C(2'), O(2'), C(3'), O(3')). 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*.

## Results

**Synthesis.** The reaction of M(CO)<sub>5</sub>THF (M = group 6 metal, produced photochemically from M(CO)<sub>6</sub> in THF) with 2 equiv of [Et<sub>4</sub>N][DTBCatH] in THF yields a product which is insoluble in THF and analyzes to be [Et<sub>4</sub>N]<sub>2</sub>[M(CO)<sub>3</sub>DTBCat]·[DTBCatH<sub>2</sub>]. This product is the result of the displacement of the THF ligand

- (3) For a recent review in this area see: Caulton, K. G. *New J. Chem.* **1994**, 18, 25.
- (4) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, 31, 3190.
- (5) Hartl, F.; Vlček, A., Jr.; deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1990**, 29, 1073.
- (6) Hartl, F.; Stufkens, D. J.; Vlček, A., Jr. *Inorg. Chem.* **1992**, 31, 1687.
- (7) Sellmann, D.; Ludwig, W.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1985**, 294, 199.
- (8) Sellmann, D.; Wilke, M.; Knoch, F. *Inorg. Chem.* **1993**, 32, 2534.
- (9) Darensbourg, D. J.; Klausmeyer, K. K.; Mueller, B. L.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 1503.
- (10) (a) Osakado, K.; Kim, Y.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, 30, 197. (b) Kim, Y.; Takanaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, 112, 1096. (c) Kegley, S. E.; Schaverien, C. J.; Fruedenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, 109, 6563. (d) Braga, D.; Sabatino, P.; DiBugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, 334, C46. (e) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, 111, 7094.
- (11) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1995**, 34, 4676.



**Figure 1.** Thermal ellipsoid drawing of the dianion of complex **2** (50% probability) with the atomic numbering scheme.

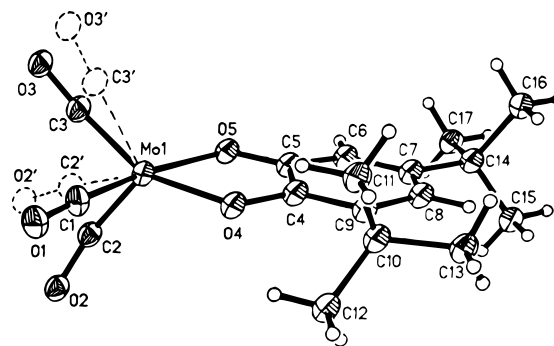
**Table 2.** Selected Bond Lengths (Å)<sup>a</sup> and Bond Angles (deg)<sup>a</sup> for **2**

W(1)–O(5)	2.151(4)	W(1)–O(6)	2.173(3)
W(1)–C(1)	1.940(5)	W(1)–C(2)	2.009(7)
W(1)–C(3)	1.951(6)	W(1)–C(4)	2.029(8)
O(1)–C(1)	1.194(7)	O(2)–C(2)	1.175(8)
O(3)–C(3)	1.182(7)	O(4)–C(4)	1.15(1)
O(5)–C(5)	1.351(6)	O(6)–C(6)	1.331(6)
O(5)–W(1)–O(6)	76.0(1)	O(5)–W(1)–C(1)	99.8(2)
O(6)–W(1)–C(1)	175.6(2)	O(5)–W(1)–C(2)	100.1(2)
O(6)–W(1)–C(2)	95.2(2)	C(1)–W(1)–C(2)	83.9(2)
O(5)–W(1)–C(3)	169.6(2)	O(6)–W(1)–C(3)	95.8(2)
C(1)–W(1)–C(3)	88.5(2)	C(2)–W(1)–C(3)	86.9(3)
O(5)–W(1)–C(4)	90.7(2)	O(6)–W(1)–C(4)	101.5(2)
C(1)–W(1)–C(4)	80.0(3)	C(2)–W(1)–C(4)	162.0(2)
C(3)–W(1)–C(4)	84.7(3)	W(1)–O(5)–C(5)	115.0(3)
W(1)–O(6)–C(6)	114.1(3)		

<sup>a</sup> Estimated standard deviations are given in parentheses.

by the deprotonated oxygen of the catechol. Subsequent loss of CO ligands and further deprotonation by the second equivalent of ligand produces the chelated product. Unlike the case of the unsubstituted catechol derivatives,<sup>9,11</sup> there was no evidence (as witnessed in the infrared spectrum) that in acetonitrile solution there was hydrogen bonding from the free DTBCatH<sub>2</sub> produced by the reaction with the metal complex. This may be the result of steric hindrance by the bulky *tert*-butyl group in the 3-position. When M = W, the product is a mixture of tricarbonyl (**2a**) and tetracarbonyl (**2**) species, as seen in the infrared spectrum where a four-band pattern for the tetracarbonyl and a two-band pattern for the tricarbonyl are observed. On the other hand, when M = Mo or Cr, the only observed product is the tricarbonyl moiety (**4** and **5**); i.e., a two-band pattern only is seen in the infrared spectrum. The extra equivalent of DTBCatH<sub>2</sub> was removed from an acetonitrile solution of the complexes by washing with a 5-fold excess of sodium methoxide followed by filtration through Celite.

**Structures.** Crystals of complex **2** suitable for a single-crystal X-ray structure determination were grown from a concentrated acetonitrile solution, by slow diffusion of diethyl ether, over a 1 week period at –10 °C. Due to the facile CO lability of this complex, an atmosphere of CO was present to force the formation of the tetracarbonyl (**2**) over that of the CO loss product, **2a**, which has already been structurally characterized.<sup>9</sup> Figure 1 shows a drawing of the dianion, and selected bond distances and angles are provided in Table 2. The structure of complex **2** consists of a W(CO)<sub>4</sub> residue chelated by DTBCat. The charge on the tungsten center is balanced by two tetraethylammonium cations. The geometry about the tungsten atom is that of a distorted octahedron; the average W–C bond length of the carbonyls *trans* to oxygen is 1.945[8] Å and the average



**Figure 2.** Thermal ellipsoid drawing of the dianion of complex **4** (50% probability) with the atomic numbering scheme.

**Table 3.** Selected Bond Lengths (Å)<sup>a</sup> and Angles (deg)<sup>a</sup> for **4**

Mo(1)–C(3)	1.87(3)	Mo(1)–C(2)	1.89(3)
Mo(1)–C(2')	1.90(3)	Mo(1)–C(1)	1.932(9)
Mo(1)–C(3')	2.00(3)	Mo(1)–O(4)	2.083(6)
Mo(1)–O(5)	2.193(6)	O(1)–C(1)	1.174(11)
O(2)–C(2)	1.29(4)	O(2')–C(2')	1.24(4)
O(3)–C(3)	1.17(4)	O(3')–C(3')	1.14(4)
O(4)–C(4)	1.348(11)	O(5)–C(5)	1.334(10)
C(3)–Mo(1)–C(2)	86(2)	C(3)–Mo(1)–C(1)	87.3(12)
C(2)–Mo(1)–C(1)	82.0(12)	C(2')–Mo(1)–C(1)	87.0(12)
C(2')–Mo(1)–C(3')	81.4(14)	C(1)–Mo(1)–C(3')	79.8(12)
C(3)–Mo(1)–O(4)	153.6(10)	C(2)–Mo(1)–O(4)	120.7(12)
C(2')–Mo(1)–O(4)	153.9(10)	C(1)–Mo(1)–O(4)	92.9(3)
C(3')–Mo(1)–O(4)	124.3(11)	C(3)–Mo(1)–O(5)	102.8(12)
C(2)–Mo(1)–O(5)	104.1(11)	C(2')–Mo(1)–O(5)	103.5(12)
C(1)–Mo(1)–O(5)	168.5(3)	C(3')–Mo(1)–O(5)	106.1(10)
O(4)–Mo(1)–O(5)	75.6(2)		

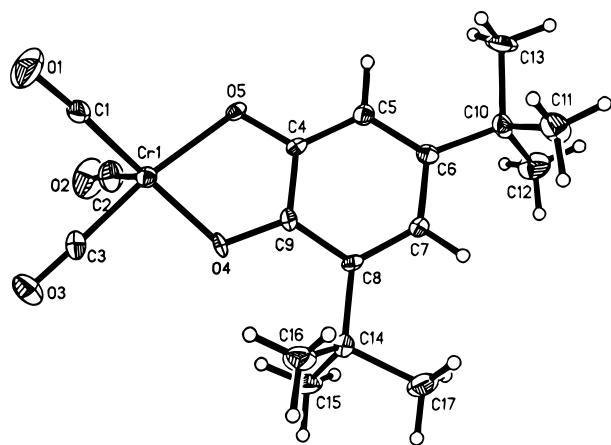
<sup>a</sup> Estimated standard deviations are given in parentheses.

W–C bond length of the carbonyls *cis* to both oxygens is 2.019–[10]. The W–O bond distances were determined to be 2.151–(4) and 2.173(3) Å, values expected for a W–O single bond. That is, W–O bond lengths observed in coordinatively and electronically saturated tungsten(0) phenoxide derivatives range from 2.168(9) to 2.191(6) Å.<sup>10e,12</sup> These W–O bond distances in **2** show a rather large lengthening from the unsaturated tricarbonyl derivative (**1**), where the distances are 2.059(6) and 2.154(6) Å. The C–O bond lengths of the chelated catechol moiety are 1.351(6) and 1.331(6) Å, which are well within the expected range for a catechol compared to those typical for a quinone or semiquinone.<sup>13</sup> The O(5)–W–O(6) bite angle is 76.0(1)°, nearly the same as that found in the unsaturated tricarbonyl analog where the angle is 75.5(4)°.

Similarly, crystals of complex **4** suitable for X-ray crystal studies were obtained from a concentrated solution of acetonitrile, as the product of slow diffusion of diethyl ether at –10 °C. Figure 2 shows a drawing of the dianion, and selected bond distances and angles are given in Table 3. The structure of **4** is another example of a zerovalent group 6 metal center which is coordinatively unsaturated. The molybdenum center is five-coordinate with a geometry intermediate between a square pyramid and a trigonal bipyramid. Two tetraethylammonium cations are present to balance the charge. Two of the carbonyl groups exhibit disorder; the Mo–C bond length of the non-disordered carbonyl is 1.932(9) Å. The Mo–O distances are 2.083(6) and 2.193(6) Å; this shows an even greater asymmetry over the tungsten analog **2a**. The C–O bond lengths of the catecholate ligand are 1.348(11) and 1.334(10) Å, confirming the assignment as a catecholate. The bite angle of the chelating

(12) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 2418.

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



**Figure 3.** Thermal ellipsoid drawing of the dianion of complex **5** (50% probability) with the atomic numbering scheme.

**Table 4.** Selected Bond Lengths (Å)<sup>a</sup> and Angles (deg)<sup>a</sup> for **5**

Cr(1)–C(2)	1.787(9)	Cr(1)–C(1)	1.778(8)
Cr(1)–C(3)	1.795(7)	Cr(1)–O(4)	1.924(7)
Cr(1)–O(5)	2.048(7)	O(1)–C(1)	1.188(12)
O(2)–C(2)	1.181(13)	O(3)–C(3)	1.194(10)
O(4)–C(9)	1.331(10)	O(5)–C(4)	1.327(10)
C(2)–Cr(1)–C(1)	90.2(9)	C(2)–Cr(1)–C(3)	79.7(9)
C(1)–Cr(1)–C(3)	85.5(7)	C(2)–Cr(1)–O(4)	122.2(8)
C(1)–Cr(1)–O(4)	146.4(8)	C(3)–Cr(1)–O(4)	91.4(4)
C(2)–Cr(1)–O(5)	104.5(7)	C(1)–Cr(1)–O(5)	101.9(5)
C(3)–Cr(1)–O(5)	171.3(4)	O(4)–Cr(1)–O(5)	79.9(3)
C(9)–O(4)–Cr(1)	116.3(5)	C(4)–O(5)–Cr(1)	112.2(5)
O(1)–C(1)–Cr(1)	175.4(12)	O(2)–C(2)–Cr(1)	177.7(14)
O(3)–C(3)–Cr(1)	172(2)	O(5)–C(4)–C(5)	123.2(8)

<sup>a</sup> Estimated standard deviations are given in parentheses.

catechol is 75.6(2)°, nearly the same as that of the tungsten tricarbonyl analog.

Crystals of **5** were obtained in 2 days by the diffusion of diethyl ether into an acetonitrile solution of the complex. Figure 3 shows a drawing of the dianion, and selected bond distances and angles are given in Table 4. The structure of **5** completes the series of zerovalent group 6 metal tricarbonyl DTBCat complexes. In this complex the average Cr–C distance of the carbonyl groups is 1.786[14] Å. The Cr–O bond distances are 2.048(7) and 1.924(7) Å, and the bite angle of the chelate is 79.9(3)°, slightly larger than those of the previous tricarbonyl examples, but consistent with the unsubstituted catecholate complexes described elsewhere.<sup>11</sup> The C–O bond distances of 1.331(10) and 1.327(10) Å are consistent with previous results.

**Spectral Properties.** The spectral properties for complexes **2** and **2a** have been previously communicated;<sup>9</sup> however, these are reiterated in Table 5 for comparative purposes. As anticipated, the molybdenum complex, **4**, exhibits a two-band pattern in the  $\nu(\text{CO})$  region of the infrared at 1870 (s) and 1731 (vs)  $\text{cm}^{-1}$ , which is consistent with a tricarbonyl derivative of approximately  $C_{3v}$  symmetry. Exposure of an acetonitrile solution of **4** to an atmosphere of CO led to the partial formation of a tetracarbonyl species as indicated by a four-band pattern in the  $\nu(\text{CO})$  region of the infrared (1972 (w), 1873 (s), 1800 (m), and 1761 (m)  $\text{cm}^{-1}$ ), along with peaks due to the tricarbonyl derivative (**4**). Nearly equal quantities of the molybdenum tetracarbonyl and tricarbonyl complexes were observed in acetonitrile solution under the above conditions. The  $^{13}\text{C}$  resonance for the three inequivalent CO ligands of complex **4** appeared at 240 ppm regardless of temperature. However, upon addition of a  $^{13}\text{CO}$  atmosphere to an acetonitrile solution of **4** at room temperature, supplementary to the  $^{13}\text{C}$  resonance at 240 ppm, a peak was observed at 218.4 ppm. Upon lowering of

**Table 5.** Spectral Data for  $[\text{Et}_3\text{N}]_2[\text{M}(\text{CO})_{4-n}(\text{DTBCat})]^-$  Derivatives in Acetonitrile Solution ( $n = 0, 1$ )

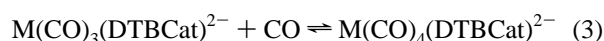
dianion <sup>a</sup>	$\nu(\text{CO}), \text{cm}^{-1}$	$^{13}\text{C}$ NMR of CO ligands, ppm
$\text{W}(\text{CO})_4(\text{DTBCat})^{2-}$ ( <b>2</b> )	1962 (w) 1815 (s), 1796 (m, sh), 1755 (m)	209.0, 219.8, 220.2
$\text{W}(\text{CO})_3(\text{DTBCat})^{2-}$ ( <b>2a</b> )	1859 (s), 1721 (vs)	234.2
$\text{W}(\text{CO})_3(\text{PMe}_3)(\text{DTBCat})^{2-}$	1849 (s), 1709 (vs)	
$\text{W}(\text{CO})_3(\text{PEt}_3)(\text{DTBCat})^{2-}$	1844 (s), 1701 (vs)	
$\text{Mo}(\text{CO})_3(\text{DTBCat})^{2-}$ ( <b>4</b> )	1870 (s), 1731 (vs)	240.0
$\text{Mo}(\text{CO})_4(\text{DTBCat})^{2-}$	1972 (w), 1837 (s), 1800 (m), 1761 (m)	209.5, 226.4
$\text{Cr}(\text{CO})_3(\text{DTBCat})^{2-}$ ( <b>5</b> )	1869 (s), 1732 (vs)	248.0

<sup>a</sup> 3,5-Di-*tert*-butylcatecholate = DTBCat.

the temperature to  $-35$  °C, the resonance at 218.4 ppm assigned to the tetracarbonyl derivative splits into two resonances of equal intensity at 209.5 and 226.4 ppm. On the basis of the observed coalescence temperature of  $-5$  °C, the rate constant for the *cis*–*trans* intramolecular CO exchange in the tetracarbonyl derivative is approximately  $4.7 \times 10^3 \text{ s}^{-1}$ . This is approximately 50 times larger than that observed for the  $\text{W}(\text{CO})_4(\text{O}_2\text{C}_6\text{H}_4)^{2-}$  species, where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were found to be  $12.0 \pm 0.7 \text{ kcal/mol}$  and  $-4.5 \pm 2.5 \text{ eu}^\circ$ .

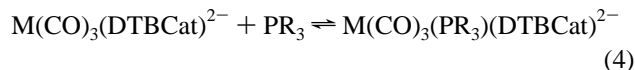
The chromium complex, **5**, also displays a two-band pattern in the infrared spectrum in  $\text{CH}_3\text{CN}$  at 1869 (s) and 1732 (vs)  $\text{cm}^{-1}$ , consistent with a tricarbonyl of approximate  $C_{3v}$  symmetry. In the presence of a CO atmosphere there was no change in the infrared spectrum, indicating no reaction of **5** with CO. Similarly, the  $^{13}\text{C}$  NMR spectrum displayed only one resonance for the tricarbonyl derivative at 248 ppm; this peak did not broaden or move upon lowering the temperature of the solution to  $-35$  °C. At all temperatures available for inspection, the three inequivalent carbonyls appear to be equivalent, demonstrating the low-energy barrier for the fluxional process. That is, the fast exchange of CO ligands, which is ubiquitous in five-coordinate metal carbonyl derivatives, is observed for all the coordinatively unsaturated dianions reported herein and elsewhere. Table 5 lists a summary of infrared and  $^{13}\text{C}$  NMR spectral data for all complexes.

**Reactivity.** The coordinatively saturated tungsten tetracarbonyl complex, **2**, is only stable in the presence of an atmosphere of carbon monoxide. Upon application of a vacuum to a solution of **2**, complete conversion to the tricarbonyl derivative, **2a**, occurs. Complex **2a** was also observed to readily decompose in methanol solution. This is presumably the result of strong hydrogen-bonding between methanol and the catecholate's oxygen atoms, which weaken the W–O bonds, and ultimately results in ligand dissociation and degradation to  $\text{W}(\text{CO})_6$ . Indeed the reduced electron donation of the catecholate ligand is noted upon dissolution of complex **2a** in acetonitrile containing 10 equiv of methanol, where the  $\nu(\text{CO})$  vibrational modes shift to higher frequencies at 1863 and 1727  $\text{cm}^{-1}$ . The molybdenum analog, complex **4**, exists in equilibrium with roughly an equal quantity of the tetracarbonyl derivative when exposed to an atmospheric pressure of CO at ambient temperature. On the contrary, the chromium derivative, **5**, is completely nonreactive toward CO at modest pressures. At high pressure ( $>700$  psi) there is some indication in the  $\nu(\text{CO})$  region of the infrared spectrum for tetracarbonyl formation prior to decomposition to  $\text{Cr}(\text{CO})_6$ . Hence, the equilibrium depicted in eq 3 at ambient temperature in the presence of 1



atm of CO lies progressively to the right as one proceeds down the row of group 6 metals, with that for chromium being essentially all the way to the left and that for tungsten all the way to the right.

The tungsten tricarbonyl complex, **2a**, was observed to react as well with phosphines. For example, the addition of 1 equiv of  $\text{PMe}_3$  yields a shift in the infrared spectrum to lower wavenumbers, from 1859 and  $1721\text{ cm}^{-1}$  to 1849 and  $1709\text{ cm}^{-1}$ . This shift is consistent with an increase in electron density at the metal center due to the binding of a basic phosphine. Reaction 4 does not go completely to the right in



the presence of 1 equiv of phosphine, suggesting that there is an equilibrium between the two species. Addition of a 5-fold excess of  $\text{PMe}_3$  results in complete conversion to the phosphine adduct as witnessed in the infrared spectrum. Attempts to grow crystals from a saturated acetonitrile solution with excess trimethylphosphine yielded crystals lacking the phosphine. The tungsten tricarbonyl also reacts with  $\text{PET}_3$ ; the infrared spectrum exhibits a shift to 1844 (s) and  $1701\text{ (vs)}\text{ cm}^{-1}$ . In this case, the equilibrium between the adduct and the starting material lies much further to the side of the unsaturated metal center; even using a 5-fold excess of  $\text{PET}_3$ , there is still a significant amount of starting material present. Use of  $\text{P}^n\text{Pr}_3$  in an excess of 10 equiv or more does not yield an appreciable amount of phosphine adduct product. It is not clear whether the decreasing reactivity is due to increased steric bulk or the increase in basicity of the phosphines. In all cases concerning these phosphines, exposure of the solution to 1 atm of CO yields complete conversion to the tetracarbonyl. That is, the phosphine is displaced from the metal center rapidly by the CO ligand. This process is also reversible; if the atmosphere of CO is removed by vacuum, the phosphine adduct reappears.

The reaction of **2a** with  $\text{PMe}_3$  can also be seen in the  $^{31}\text{P}$  NMR spectrum. At room temperature with 1 equiv of phosphine a resonance is observed at  $-41\text{ ppm}$  relative to  $\text{H}_3\text{PO}_4$ . This is a shift of 20 ppm from free  $\text{PMe}_3$  at  $-61\text{ ppm}$ . As might be expected, this resonance is a time-averaged signal of bound and unbound phosphine. Lowering the temperature of the solution to  $10\text{ }^\circ\text{C}$  yields a shift in the spectrum to  $-38\text{ ppm}$ , demonstrating a shift in the equilibrium toward more phosphine being bound to the metal center. This trend in shifts continues as the temperature is lowered to  $-30\text{ }^\circ\text{C}$ , where the resonance is observed as a broad signal at  $-31\text{ ppm}$ . The reverse trend is also observed by raising the temperature; that is, when the solution is heated to  $50\text{ }^\circ\text{C}$ , the resonance is shifted to  $-51\text{ ppm}$ , indicating that the equilibrium described by eq 4 has been displaced to the left. The interaction of  $\text{PMe}_3$  with **2a** is enhanced in the presence of hydrogen-bonding reagents such as methanol. However, with time, decomposition of the complex occurs under these conditions (*vide supra*). On the other hand, the reaction of complex **2a** with a good  $\pi$ -acid such as  $\text{P}(\text{OMe})_3$  is markedly different from that observed for the good  $\sigma$ -donor  $\text{PMe}_3$ . When  $\text{P}(\text{OMe})_3$  is added to an acetonitrile solution of **2a**, there is no observable shift in the  $\nu(\text{CO})$  infrared spectrum. This lack of reactivity is also seen in the  $^{31}\text{P}$  NMR spectrum, over the temperature range  $-20$  to  $+20\text{ }^\circ\text{C}$ , where there is no change in the resonance position for free  $\text{P}(\text{OMe})_3$  at  $141\text{ ppm}$  relative to  $\text{H}_3\text{PO}_4$ . There is however a reaction when 10 equiv of the hydrogen-bonding agent methanol is added to the solution. At  $0\text{ }^\circ\text{C}$  in the  $^{31}\text{P}$  NMR spectrum, there appears a resonance at  $152\text{ ppm}$ ; this peak has accompanying tungsten satellites with  $J_{\text{W-P}}$  of  $356\text{ Hz}$ . By way of contrast, the

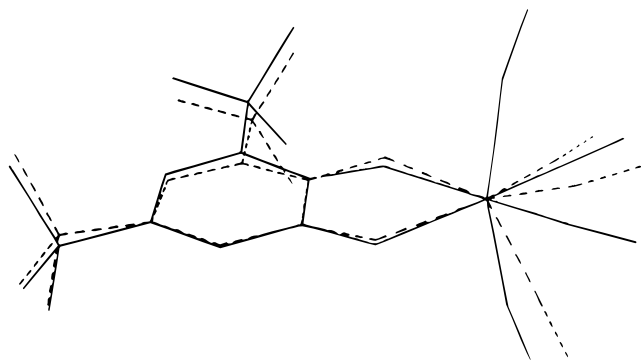


Figure 4. Superposition of stick drawings of the dianions of complexes **2** and **2a**.

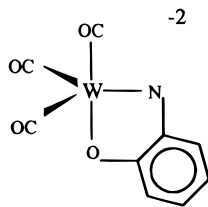
molybdenum and chromium tricarbonyl derivatives, **4** and **5**, were unreactive with either phosphines or phosphites over temperature ranges analogous to those examined for the tungsten derivative.

## Discussion

The crystal structures of **4** and **5** permit a comparison of these structures with that of the tungsten derivative **2a**. The most important feature of these complexes is the asymmetry in the M–O bond lengths. For **2a**, these bond lengths are 2.154(6) and 2.059(6) Å, a difference of 0.095 Å. For the molybdenum complex **4** this variance is larger with Mo–O distances of 2.193(6) and 2.083(6) Å, for a difference of 0.110 Å. With the chromium analog, **5**, the disparity is slightly larger, yet with Cr–O distances of 2.048(7) and 1.924(7) Å, thus providing a difference of 0.124 Å. Concomitantly, there is an increase in the bite angle from  $75.2(2)^\circ$  for **2a**, to  $75.6(2)^\circ$  for **4**, to  $79.9(2)^\circ$  for **5**. The large increase in bite angle in going from Mo to Cr may be attributed to the large decrease in size of 4d vs 3d orbitals. The geometries of the carbonyl ligands around the metal centers are similar for the three structures. There is one carbonyl which is nearly *trans* to the less donating oxygen (longer M–O bond) of the catecholate with O–M–C bond angles of  $166.7(3)^\circ$  for **2a**,  $168.5(3)^\circ$  for **4**, and  $171.3(4)^\circ$  for **5**. The more donating oxygen (shorter M–O bond) forms a plane with the other two carbonyl ligands and the metal center with deviations from planarity of 0.026 Å for **2a** and 0.038 Å for **5**; these carbonyls are disordered in **4**, making a comparison difficult.

The geometry of the five-coordinate derivatives is best described as intermediate between trigonal bipyramidal and square planar. For example, see Figure 4, which overlays the structures of the  $-\text{W}(\text{CO})_3$  and  $-\text{W}(\text{CO})_4$  catecholate dianions. It is obvious from this drawing that structural changes in addition to simple displacement of a CO ligand from the tetracarbonyl complex occur upon formation of the tricarbonyl complex. Nevertheless, it is easiest to visualize the structures of the metal dianions reported herein as consisting of an approximate trigonal plane made up of one oxygen atom of the catecholate (involving the shortest M–O bond), two carbonyl ligands, and the metal center. An apical carbonyl ligand and the other catecholate oxygen atom complete the metal's coordination sphere. It should be noted that the short metal–oxygen bond in each instance involves the more basic oxygen atom, that which is *ortho* to the electron-releasing *tert*-butyl substituent of the catecholate ligand. It is also important to note that, in the unsubstituted catecholate chromium derivative,  $\text{Cr}(\text{CO})_3(\text{O}_2\text{C}_6\text{H}_4)_2^{2-}$ , the Cr–O bond lengths are much less dissimilar, at 1.992(9) and 2.003(9) Å. A similar observation has been reported for the unsubstituted and symmetrically substituted

dithiolate derivatives.<sup>7,8</sup> On the other hand, the structure of  $[\text{Et}_4\text{N}]_2[\text{W}(\text{CO})_3\text{OC}_6\text{H}_4\text{NH}]$  reveals a trigonal plane of tungsten, two CO ligands, and the amido group (deviation from planarity of only 0.005 Å).<sup>14</sup> Interestingly, the W–N bond is short (2.078 Å) and the W–O bond length of 2.143 Å is only a bit shorter than a single bond. This observation is consistent with the amido ligand being the better  $\pi$ -donating group.



The well-defined structures of the DTBCatW(CO)<sub>4</sub><sup>2-</sup> (**2**) and –W(CO)<sub>3</sub><sup>2-</sup> (**2a**) derivatives allow for an accurate comparison of the W–O bond lengths in proceeding from the coordinatively saturated to coordinatively unsaturated metal center. The W–O bond, which is *ortho* to the electron-donating *tert*-butyl substituent, is significant shorter (2.059(6) Å) than the other W–O bond (2.154(6) Å). The latter bond length is only slightly compressed relative to the corresponding W–O single bond lengths in **2** of 2.151(4) and 2.173(3) Å.

### Conclusions

Several themes are emerging from our studies of these formally “16-electron”, coordinatively unsaturated group 6 metal catecholates. First, the thermodynamic stability of five-coordinate complex in the presence of CO relative to the six-coordinate derivative decreases as one proceeds down the

periodic table. Furthermore, the stability of the coordinatively unsaturated catecholate metal dianion is a function of substituents on the aromatic ring, with electron-releasing groups stabilizing the five-coordinate complex. Similar observations have been noted as well for group 7 metal analogs.<sup>5</sup> Second, if the structures of these five-coordinate dianions are loosely defined as trigonal bipyramidal, the more basic oxygen ligand occupies an equatorial site as indicated by a short M–O bond. Furthermore, the propensity of the oxygen atoms of the catecholate for  $\pi$ -donating to the metal center can be mediated by interactions with electrophiles, such as hydrogen-bonding reagents. It is noteworthy that an enhancement in  $\pi$ -donating ability is seen in going from Cr(CO)<sub>3</sub>(S<sub>2</sub>C<sub>6</sub>R<sub>4</sub>)<sup>2-</sup> to Cr(CO)<sub>3</sub>(O<sub>2</sub>C<sub>6</sub>R<sub>4</sub>)<sup>2-</sup> as evidenced by the reversible, facile reaction of the benzene-1,2-dithiolates with CO to provide the coordinatively saturated tetracarbonyl derivatives and the lack of such reaction with the analogous catecholates.<sup>7,8,11,15</sup> Finally, it is apparent as well that these conclusions hold for other related group 6 and group 7<sup>5</sup> metal derivatives. For example, we have obtained X-ray structures of coordinatively unsaturated tungsten carbonyl derivatives derived from aminophenol and diaminobenzene. These complexes will form the basis of a later report.

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**Supporting Information Available:** Tables of atomic coordinates and isotropic displacement parameters, anisotropic thermal parameters, and complete bond lengths and angles for complexes **2**, **4**, and **5** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1535.

(15) Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297.