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Dicyclopentadienyldi-*tert*-butoxydichromium. Preparation, Properties, Structure, and Reactions with Small Unsaturated Molecules

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Hydrocarbon solutions of chromocene react rapidly with alcohols, ROH, to give polymeric chromium(II) alkoxides $(Cr(OR)_2)_x$, where R = Me, Et, and *t*-Pr. The more sterically demanding and less acidic *t*-BuOH and R_3SiOH (R = Me and Ph) react more slowly and lead to products of empirical formula $CpCrO-t-Bu$ and $CpCrOSiR_3$, respectively. The *tert*-butoxide complex, characterized by a number of physical techniques including single-crystal X-ray crystallography, is dinuclear, $Cp_2Cr_2(O-t-Bu)_2$, with a nonplanar central $(Cr-\mu-O)_2$ moiety and a Cr-Cr distance of 2.65 (2) Å. It is reactive toward a number of small unsaturated molecules including acetylenes, carbon monoxide, carbon dioxide, nitric oxide, and nitrous oxide. The reaction between CO_2 and $Cp_2Cr_2(O-t-Bu)_2$ in THF leads to chromocene and $Cr_2(O_2CO-t-Bu)_4(THF)_2$ which has been structurally characterized by single-crystal X-ray crystallography. $Cr_2(O_2CO-t-Bu)_4(THF)_2$ has the dichromium tetraacetate structure with a Cr-Cr distance of 2.367 (3) Å and axially coordinated THF molecules. The principal crystallographic data for $Cp_2Cr_2(O-t-Bu)_2$ are space group $P2_1/n$, $a = 15.102$ (4) Å, $b = 18.712$ (4) Å, $c = 14.413$ (3) Å, $\beta = 104.40$ (2)°, $V = 3945$ (2) Å³, and $Z = 8$. The principal crystallographic data for $Cr_2(O_2CO-t-Bu)_4(THF)_2$ are space group $P2_1/c$, $a = 10.011$ (1) Å, $b = 9.852$ (2) Å, $c = 19.477$ (3) Å, $\beta = 104.74$ (1)°, $V = 1857$ (1) Å³, and $Z = 2$.

Introduction

Paramagnetic organometallic compounds violate the 16–18 electron rule² and their reactivity patterns are not well understood. Fluxional and other dynamic solution processes are presently unknown and in most instances cannot be investigated by NMR spectroscopy. However, a number of early transition-metal paramagnetic compounds are implicated in catalytically important processes, and an ever increasing number of organometallic reactions involving diamagnetic complexes are being found to proceed via electron-transfer and free-radical pathways.³ Both of these factors should stimulate research involving paramagnetic organometallics.

Knowing that chromocene deposited on dehydrated silica serves as an excellent catalyst for the polymerization of ethylene⁴ and suspecting that the active species could be represented as Cp–Cr–OSi(support), we initiated a study of the reactions of chromocene with alcohols and trialkylsilanols. Herein we report these studies, including a detailed characterization of the dinuclear compounds $Cp_2Cr_2(O-t-Bu)_2$ and $Cr_2(O_2CO-t-Bu)_4(THF)_2$, as well as a number of preliminary studies concerning reactions of the former with small unsaturated molecules.

Experimental Section

General procedures have been described.⁵ Dry and oxygen-free atmospheres and solvents were used throughout.

Chromocene was prepared by the reaction between $CrCl_3$ and LiC_5H_5 (from LiBu and Cp-H) in THF/hexane solvent mixtures and was purified by sublimation.

Preparation of Dicyclopentadienyldi-*tert*-butoxydichromium. Chromocene (4.91 mmol) and *tert*-butyl alcohol (7.36 mmol) were refluxed together in toluene (35 mL) for 5 h. The solvent was stripped and the compound sublimed (140 °C (10^{-3} torr)) overnight to yield dark red crystals of $(C_5H_5)_2Cr_2(\mu-O-t-Bu)_2$ in 84% yield based on Cr. Anal. Calcd for $C_{18}H_{28}O_4Cr_2$: C, 56.86; H, 7.37. Found: C, 56.6; H, 7.2.

IR data obtained from a Nujol mull between CsI plates in the region 3100–200 cm^{-1} : 3091 (m), 2394 (w), 2259 (2), 1751 (m, br), 1667 (m), 1631 (m), 1528 (w), 1422 (m, sh), 1357 (vs), 1259 (w), 1237 (s), 1178 (vs, br), 1112 (m, sh), 1061 (w), 1010 (vs), 997 (vs), 934 (vs, br), 874 (m), 842 (m, sh), 770 (vs, br), 592 (vs), 497 (s), 462 (m), 400 (vs), 359 (s), 324 (vs), 238 (m), 222 (w).

Mass spectral data obtained using the method of direct insertion at 110 °C: m/e 380, $(Cr_2(C_5H_5)_2(OC(CH_3)_3)_2)^+$, medium; m/e 323, $(Cr_2(C_5H_5)_2(OC(CH_3)_3)(O))^+$, large; m/e 267, $(Cr_2(C_5H_5)_2(OH)(O))^+$, base peak; m/e 250, $(Cr_2(C_5H_5)_2(O))^+$, medium; m/e 233, very small; m/e 214, small; m/e 200, $(Cr(C_5H_5)_2(OH_2))^+$, small; m/e 189, $(Cr(C_5H_5)(O)(CH_3)_2C=CH_2)^+$, very small.

Magnetic susceptibility data (μ_{eff} (μ_B) per Cr atom (average value of two determinations on 0.0322 and 0.0488 M solutions)) obtained from toluene solution by the method of Evans⁶ and temperatures (T ,

K): 1.88 (333.5), 1.84 (316), 1.77 (293), 1.73 (278), 1.67 (255), 1.57 (228.5), 1.49 (214). The differences between the values obtained at the two concentrations were insignificant.

The visible spectrum in hexane shows absorptions at $\lambda_{max} = 5200$ Å (ϵ 600) and 6675 Å (ϵ 100). Molecular weight (freezing benzene): 365, 370 (theory for dimer: 380).

Preparation of Dicyclopentadienyldi-*tert*-butoxydinitrosyldichromium. To a solution of $(C_5H_5)_2Cr_2(\mu-O-t-Bu)_2$ (4.13 mmol) in pentane (20 mL) was added a total of 8.66 mmol of NO in two equal portions at –196 °C. After each addition, the mixture was allowed to warm to room temperature; the solution was then stirred overnight. The solvent was stripped and the mixture sublimed (150 °C (10^{-3} torr)) overnight to give yellowish green crystals of $(C_5H_5)_2Cr_2(O-t-Bu)_2(NO)_2$ in 46% yield based on Cr. Anal. Calcd for $C_{18}H_{28}O_4N_2Cr_2$: C, 49.09; H, 6.41; N, 6.36. Found: C, 49.1; H, 6.49; N, 6.49.

IR data obtained from a Nujol mull between CsI plates in the region 3300–200 cm^{-1} : 3231 (w), 2265 (w), 1742 (m), 1637 (vs, br), 1365 (vs), 1245 (m), 1233 (m), 1175 (vs), 1129 (w), 1069 (w), 1018 (s), 897 (vs, br), 845 (s), 815 (vs), 795 (vs), 768 (s), 637 (s), 617 (s), 594 (s), 568 (m), 549 (m), 500 (m), 476 (w), 447 (m), 414 (s), 370 (m, br), 286 (m), 275 (m), 255 (m). ¹H NMR (benzene, 30 °C): τ 7.7–10.5 (br, CH_3). The compound is apparently paramagnetic. The molecular weight is 441 (one determination) in freezing benzene (theory for dimer: 440).

Mass spectral data obtained by the method of direct insertion at 110 °C: m/e 440, $((C_5H_5)_2Cr_2(OC(CH_3)_3)_2(NO)_2)^+$; m/e 410, $((C_5H_5)_2Cr_2(OC(CH_3)_3)_2NO)^+$; m/e 380, $((C_5H_5)_2Cr_2(OC(CH_3)_3)_2)^+$.

Reaction of $(C_5H_5)_2Cr_2(O-t-Bu)_2$ with CO_2 and THF. To a solution of $(C_5H_5)_2Cr_2(O-t-Bu)_2$ (2.51 mmol) in pentane/THF (2:1) (30 mL) was added CO_2 (7.53 mmol) at –198 °C. The closed system was allowed to stand for 72 h. The mixture was filtered, and the filtrate was washed with pentane (40 mL) to give red crystals of $Cr_2(O_2CO-t-Bu)_4(THF)_2$ in 40–50% yield based on Cr (80–100% of theoretical yield). The filtrate yielded chromocene upon drying and sublimation (80 °C (10^{-3} torr)), which was identified by its infrared spectrum. Anal. Calcd for $C_{28}H_{52}O_{14}Cr_2$: C, 46.92; H, 7.31. Found: C, 46.3; H, 6.81.

IR data obtained from a Nujol mull between CsI plates in the region 2500–200 cm^{-1} : 2465 (w, br), 2169 (w), 1963 (w, br), 1833 (w), 1382 (vs), 1256 (s), 1245 (s), 1164 (vs), 1086 (s), 1048 (s), 1033 (s), 918 (m), 890 (s, br), 814 (s), 789 (m), 742 (s), 671 (w), 601 (s), 598 (s), 480 (s), 439 (s), 393 (m), 362 (w), 309 (s), 291 (m).

Synthesis of $[Cr_2(O-t-Bu)_2(C_5H_5)_2(C_4F_6)]_x$. A solution of $Cp_2Cr_2(O-t-Bu)_2$ (1.29 mmol) in hexanes (300 mL) was partly evacuated and exposed to an excess (5 mmol) of hexafluoro-2-butyne for 9 h using a vacuum manifold. The flask was then cooled until a total of 3.30 mmol of C_4F_6 had been added. After the flask was closed off, the solution was allowed to warm to room temperature and was stirred 1 h. The resulting solution was evaporated under vacuum, and the dried solids were extracted with diethyl ether (50 mL). The extract was filtered to remove insoluble impurities and then

dried to give a crude product which was purified by sublimation (125–130 °C (10^{-3} torr)) using a cold finger cooled by liquid nitrogen, giving the deep purple, crystalline compound $[\text{Cr}_2(\text{O}-t\text{-Bu})_2(\text{C}_5\text{H}_5)_2(\text{C}_4\text{F}_6)]_x$ in 20–30% yield based on Cr. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{Cr}_2\text{O}_2\text{F}_6$: C, 48.71; H, 5.20; F, 21.01. Found: C, 48.9; H, 5.34; F, 20.9.

IR data obtained from a Nujol mull between CsI plates in the region 3200–200 cm^{-1} : 3121 (w, br), 1737 (w, br), 1550 (m), 1502 (s), 1364 (s), 1199 (vs, br), 1164 (vs), 1111 (vs), 1094 (vs, br), 762 (s), 665 (s, sh), 634 (m, sh), 596 (vs), 522 (m), 467 (m), 416 (s), 373 (s), 347 (s), 312 (s), 247 (m), 216 (m).

Mass spectral data obtained using a probe at 170 °C: m/e 542, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)_2\text{C}_4\text{F}_6)^+$, small; m/e 523, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)_2\text{C}_4\text{F}_5)^+$, very small; m/e 485, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)(\text{O})\text{C}_4\text{F}_6)^+$, small; m/e 469, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)_2\text{C}_4\text{F}_6)^+$, very small; m/e 399, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)_2\text{F})^+$, medium; m/e 380, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)_2)^+$, large; m/e 323, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{OC}(\text{CH}_3)_3)(\text{O}))^+$, strong; m/e 269, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{O})(\text{F}))^+$, medium; m/e 267, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{O})(\text{OH}))^+$, large; m/e 250, $(\text{Cr}_2(\text{C}_5\text{H}_5)_2(\text{O}))^+$, medium; m/e 204, $(\text{Cr}(\text{C}_5\text{H}_5)(\text{COCF}_3))^+$, medium; m/e 190, $(\text{Cr}(\text{C}_5\text{H}_5)(\text{OC}(\text{CH}_3)_3))^+$, base peak; m/e 162, $(\text{C}_4\text{F}_6)^+$, medium; m/e 143, $(\text{C}_4\text{F}_5)^+$, medium; m/e 124, $(\text{C}_4\text{F}_4)^+$, small. Molecular weight (freezing benzene): 643, 709 (calculated for dimer, $\text{C}_{22}\text{H}_{28}\text{O}_2\text{F}_6\text{Cr}_2$: 542). The high value obtained may be due to the presence of some undissolved solids.

Reaction of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ with CO. Carbon monoxide (98.1 mmol) was passed through a solution of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ (3.07 mmol) in toluene/THF (6.5:1, 75 mL). The closed system was allowed to stand for 26 h. The mixture was filtered, and the filtrate was washed with pentane (40 mL) to give light greenish blue crystals. The product was somewhat soluble in THF, barely soluble in diethyl ether, and insoluble in hydrocarbons. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{Cr}$: C, 53.66; H, 5.83. Found: C, 54.4; H, 5.73.

IR data obtained from a Nujol mull between CsI plates in the region 3100–200 cm^{-1} : 3090 (w), 1901 (m, sh), 1890 (s), 1801 (s, sh), 1769 (vs), 1745 (vs), 1307 (m, br), 1263 (m), 1238 (m, br), 1179 (s), 1168 (s), 1112 (m), 1012 (m), 918 (m), 833 (m), 815 (s), 788 (m), 768 (m), 691 (w), 651 (m), 613 (s), 562 (w), 547 (w), 508 (w), 496 (w), 468 (w), 411 (w), 331 (w), 240 (w). The compound appears to be paramagnetic in THF solution. It is not volatile at 175 °C (10^{-2} torr).

Crystallographic Study of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$. Crystals of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ were grown by sublimation in vacuo in a sealed glass tube at ca. 80 °C. A large, dark red crystal measuring ca. 0.25 × 0.50 × 0.60 mm was embedded in epoxy cement and sealed in a thin-walled glass capillary. The crystal was judged to be of good quality on the basis of ω scans of several intense reflections which had peak widths at half-height of $<0.2^\circ$. Lattice constants and axial photographs indicated that the crystal belonged to the monoclinic system. Accurate values of the lattice constants and the orientation matrix used for data collection were calculated from the setting angles of 15 intense reflections having $22^\circ < 2\theta(\text{MoK}\alpha) < 29^\circ$. The lattice constants are $a = 15.102(4) \text{ \AA}$, $b = 18.712(4) \text{ \AA}$, $c = 14.413(3) \text{ \AA}$, $\beta = 104.40(2)^\circ$, and $V = 3945(2) \text{ \AA}^3$, based on a wavelength of 0.710730 Å for Mo K α X-rays. The observed volume is consistent with that anticipated for $Z = 8$.

The intensity data were collected at $23 \pm 1^\circ \text{C}$ using a Syntex PI autodiffractometer equipped with an incident-beam graphite-crystal monochromator, using Mo K α radiation. Variable scan rates from 4.0 to 24.0°/min were used for θ - 2θ scans ranging from $2\theta(\text{MoK}\alpha_1) - 0.9^\circ$ to $2\theta(\text{MoK}\alpha_2) + 0.9^\circ$ with the ratio of background to scan time equal to 0.5. A total of 5624 reflections having $0^\circ < 2\theta < 45^\circ$ were recorded. The intensities of three standard reflections measured after every 97 reflections showed a nearly linear intensity drop of 26% over the course of data collection. The data were reduced to a set of relative $|F_o|^2$ values and corrected for crystal decay. Data were not corrected for absorption ($\mu = 11.5 \text{ cm}^{-1}$). Nonunique and systematically absent data were rejected leaving 5195 reflections of which those 2113 that had $I > 3\sigma(I)$ were used for structure solution and refinement.

The systematic absences of $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) were noted, uniquely determining the space group to be $P2_1/n$, a nonstandard setting of $P2_1/c$. The observed volume and space group require that the asymmetric unit consist of two independent $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ molecules.

Structure Solution. The Patterson map was quite complex as expected with four unique chromium atoms per asymmetric unit.

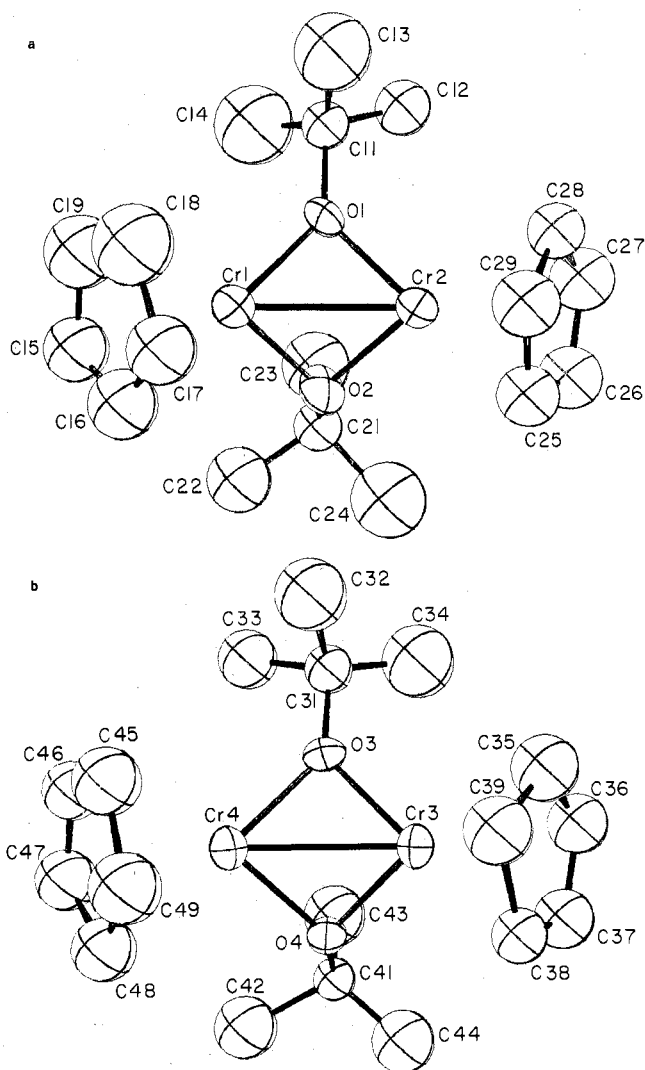


Figure 1. View of $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ using 50% probability ellipsoids and spheres and showing the atom labeling scheme: (a) molecule I, (b) molecule II.

Direct methods (MULTAN) were used to determine the positions of the four independent chromium atoms. The remaining nonhydrogen atoms were located using standard heavy-atom techniques. Least-squares refinement utilized anisotropic thermal parameters for the chromium and oxygen atoms and isotropic thermal parameters for the carbon atoms. As refinement proceeded, it became evident that many of the parameters were oscillating, and a dampening factor of 0.6 was applied to all shifts. This prompted us to examine the possibility that the two unique molecules might be crystallographically related, especially since they are essentially identical (see Figure 1a, b). Reexamination of the raw data, axial photos, and cell constants (with TRACER, a Delauney reduction routine) indicated that no higher symmetry existed and supported our choice of unit cell. However, certain classes of reflections are only poorly represented and it should be noted that considerably fewer reflections were "observed" than one would ordinarily expect from a crystal of this size and quality. We concluded that there are some "near" symmetry elements that caused complications in the final stages of refinement.

Final discrepancy indices were $R_1 = (\sum w||F_o| - |F_c||) / \sum |F_o| = 0.085$ and $R_2 = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2} = 0.110$. The esd of an observation of unit weight was 2.15. A final difference Fourier map showed no peaks of structural significance. The largest peaks were in the region of the *t*-Bu groups and ascribed to anisotropy of the methyl groups.

Crystallographic Study of $\text{Cr}_2(\text{O}_2\text{CO}-t\text{-Bu})_4(\text{THF})_2$. A crystal of $\text{Cr}_2(\text{O}_2\text{CO}-t\text{-Bu})_4(\text{THF})_2$ measuring ca. 0.2 × 0.3 × 0.4 mm was mounted in a thin-walled glass capillary embedded in epoxy cement. Crystal quality was judged to be good on the basis of ω scans of several low-angle intense reflections which had peak widths at half-height

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.3167 (2)	0.1220 (1)	0.2844 (2)	3.7 (1)	3.1 (1)	3.6 (1)	0.3 (1)	0.54 (9)	-0.2 (1)
Cr(2)	0.2246 (2)	0.2205 (1)	0.1696 (2)	4.2 (1)	2.7 (1)	3.3 (1)	-0.5 (1)	0.33 (9)	0.0 (1)
Cr(3)	0.7818 (2)	0.4739 (1)	0.3269 (2)	3.9 (1)	2.9 (1)	2.8 (1)	-0.1 (1)	0.31 (9)	-0.5 (1)
Cr(4)	0.6863 (2)	0.3755 (1)	0.2092 (2)	2.9 (1)	2.9 (1)	3.7 (1)	-0.6 (1)	0.24 (9)	0.1 (1)
O(1)	0.2746 (8)	0.2167 (5)	0.3048 (7)	6.7 (6)	2.1 (4)	3.4 (5)	1.2 (5)	0.3 (4)	-0.6 (4)
O(2)	0.1997 (7)	0.1187 (5)	0.1854 (8)	3.8 (5)	3.0 (5)	5.9 (6)	-1.2 (4)	0.2 (4)	0.6 (5)
O(3)	0.7238 (7)	0.4744 (5)	0.1895 (6)	4.8 (5)	3.0 (5)	2.4 (4)	-0.1 (5)	-0.1 (4)	0.8 (4)
O(4)	0.8027 (6)	0.3713 (5)	0.3094 (7)	2.9 (4)	2.3 (4)	3.9 (5)	0.9 (4)	-0.4 (4)	-0.1 (4)

atom	x	y	z	$B, \text{Å}^2$	atom	x	y	z	$B, \text{Å}^2$
C(11)	0.286 (1)	0.2678 (9)	0.383 (1)	4.2 (4)	C(31)	0.715 (1)	0.5246 (9)	0.114 (1)	4.3 (4)
C(12)	0.212 (1)	0.3230 (11)	0.367 (1)	6.0 (5)	C(32)	0.623 (2)	0.5595 (13)	0.104 (2)	8.5 (6)
C(13)	0.375 (2)	0.3095 (14)	0.390 (2)	9.5 (7)	C(33)	0.700 (1)	0.4826 (12)	0.019 (1)	6.9 (5)
C(14)	0.269 (2)	0.2252 (19)	0.467 (2)	12.9 (10)	C(34)	0.794 (2)	0.5785 (15)	0.142 (2)	10.4 (8)
C(15)	0.390 (1)	0.0173 (12)	0.345 (2)	7.3 (6)	C(35)	0.760 (1)	0.5831 (12)	0.389 (1)	6.8 (5)
C(16)	0.400 (1)	0.0271 (12)	0.251 (2)	7.5 (6)	C(36)	0.849 (1)	0.5700 (11)	0.418 (1)	6.0 (5)
C(17)	0.446 (1)	0.0844 (12)	0.240 (1)	6.7 (5)	C(37)	0.860 (1)	0.5114 (11)	0.479 (1)	5.7 (5)
C(18)	0.474 (2)	0.1175 (14)	0.334 (2)	9.4 (7)	C(38)	0.783 (1)	0.4861 (9)	0.489 (1)	4.4 (4)
C(19)	0.442 (2)	0.0766 (13)	0.396 (2)	8.6 (7)	C(39)	0.704 (1)	0.5308 (11)	0.430 (1)	6.3 (5)
C(21)	0.116 (1)	0.0841 (10)	0.184 (1)	5.0 (4)	C(41)	0.887 (1)	0.3355 (8)	0.309 (1)	3.7 (3)
C(22)	0.133 (2)	0.0035 (14)	0.199 (2)	8.8 (7)	C(42)	0.862 (2)	0.2536 (13)	0.279 (2)	7.9 (6)
C(23)	0.073 (2)	0.1102 (16)	0.260 (2)	10.9 (8)	C(43)	0.921 (2)	0.3622 (13)	0.225 (2)	8.6 (7)
C(24)	0.059 (2)	0.0844 (16)	0.075 (2)	11.7 (9)	C(44)	0.948 (2)	0.3378 (13)	0.405 (2)	7.9 (6)
C(25)	0.242 (1)	0.2361 (10)	0.016 (1)	5.3 (4)	C(45)	0.527 (1)	0.3712 (11)	0.165 (1)	6.6 (5)
C(26)	0.149 (1)	0.2651 (11)	0.020 (1)	6.5 (5)	C(46)	0.561 (1)	0.3344 (10)	0.098 (1)	5.5 (4)
C(27)	0.165 (1)	0.3234 (11)	0.085 (1)	6.6 (5)	C(47)	0.607 (1)	0.2771 (11)	0.136 (1)	6.0 (5)
C(28)	0.262 (1)	0.3305 (9)	0.114 (1)	4.6 (4)	C(48)	0.611 (1)	0.2749 (11)	0.240 (1)	6.1 (5)
C(29)	0.301 (1)	0.2797 (11)	0.069 (1)	5.9 (5)	C(49)	0.557 (1)	0.3317 (12)	0.254 (1)	7.0 (5)

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

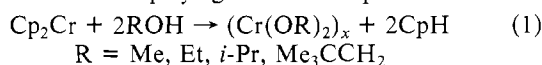
of 0.2° . Cell constants and axial photographs indicated that the crystal belonged to the monoclinic system with $a = 10.011$ (1) Å, $b = 9.852$ (2) Å, $c = 19.477$ (3) Å, $\beta = 104.74$ (1) $^\circ$, and $V = 1857.8$ (6) Å³. The observed volume was consistent with that expected for $Z = 2$. Data were collected as for $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$, with 2555 unique reflections having $2\theta \leq 45.0^\circ$ measured. Three standard reflections showed a nearly linear decrease in intensity of 14% over the period of data collection. The data were reduced to a set of relative $|F_o|^2$ values and corrected for crystal decay. No absorption correction was applied ($\mu = 13.4 \text{ cm}^{-1}$). The 1205 reflections having $I > 3\sigma(I)$ were retained as observed and used in subsequent structure solution and refinement. Systematic absences, $0k0$ ($k = 2n$) and $h0l$ ($l = 2n$), uniquely determined the space group to be $P2_1/c$.

The structure was solved using standard heavy-atom methods and refined to convergence using anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were not located. The final discrepancy indices were $R_1 = 0.071$ and $R_2 = 0.087$. The error in an observation of unit weight was 1.73. A final difference Fourier map showed no peaks of chemical significance.

All crystallographic computations were carried out on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, using the Enraf-Nonius structure determination package. Tables of structure factors are available as supplementary material.

Results and Discussion

Synthesis of CpCrOR Compounds. Hydrocarbon solutions of chromocene react rapidly with primary and secondary alcohols to yield polymeric chromium(II) alkoxides according to eq 1. Reactions employing less than 2 equiv of the alcohol



produced mixtures of $(\text{Cr}(\text{OR})_2)_x$ and unreacted chromocene. However, the bulky and less acidic *tert*-butyl alcohol reacted more slowly, and even in the refluxing toluene only partial replacement of Cp by OR was achieved as indicated by eq 2.



A similar situation was observed for the silanols Me_3SiOH and Ph_3SiOH . The compounds of empirical formula CpCrOR ,

where $\text{R} = \text{Me}_3\text{C, Me}_3\text{Si, and Ph}_3\text{Si}$, are all dark red, crystalline solids. The *tert*-butoxide complex was considered to be representative of this group and was characterized in detail.

$\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$. The dark red, crystalline compound $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ is an *extremely* air-sensitive compound. Its color arises from intense absorptions in the visible region: $\lambda_{\text{max}} = 5200$ Å (ϵ 600) and 6675 Å (ϵ 100). It is volatile and thermally stable and may be sublimed at $90\text{--}100^\circ\text{C}$ (10^{-4} cm Hg). In the mass spectrometer the ion of highest mass corresponds to the molecular ion $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2^+$ though many other Cr_2 -containing ions were observed. A cryoscopic molecular weight determination in benzene, 365 ± 15 , indicated the dinuclear species $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$, for which $M_r = 380$. Magnetic susceptibility measurements in toluene in the temperature range $+90$ to -60°C gave a temperature-independent value for χ_M' , of about 3×10^{-3} cgsu, which is indicative of strong antiferromagnetic coupling between the neighboring chromium atoms. Complete spectroscopic and magnetic susceptibility data have been given in the Experimental Section.

We were not aware of any structural studies on dinuclear chromium compounds of empirical formula CpCrX , where X is a uninegative ligand, and so we proceeded directly toward a single-crystal X-ray study of this interesting compound, using crystals grown by sublimation.

The solid compound is composed of discrete $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2$ molecules. Perspective views of the two independent molecules showing the coordination geometry and atom labeling scheme are depicted in Figure 1a,b. The final atomic coordinates and thermal parameters are listed in Table I. Bond lengths and angles are given in Tables II and III. Although the two molecules are crystallographically independent, comparison of related bond distances and angles shows them to be essentially equivalent. The molecules possess an approximate mirror plane perpendicular to the Cr-Cr bond.

Comparisons with $\text{Cp}_2\text{Cr}_2(\text{NO})_2\text{X}_2$ Compounds. As indicated previously, we are not aware of any other compounds of the type $\text{Cp}_2\text{Cr}_2\text{X}_2$ ($\text{X} =$ a uninegative group). However, a

Table II. Bond Distances (Å) in Cp₂Cr₂(O-*t*-Bu)₂^a

atoms	molecule I	molecule II
Cr1-Cr2	2.632 (5)	2.669 (6)
-O1	1.93 (1)	1.96 (1)
-O2	1.98 (1)	1.97 (1)
Cr2-O1	1.91 (1)	1.98 (1)
-O2	1.97 (1)	1.98 (1)
Cr1-C15	2.31 (2)	2.31 (2)
-C16	2.29 (2)	2.29 (2)
-C17	2.32 (2)	2.36 (2)
-C18	2.30 (2)	2.35 (1)
-C19	2.32 (2)	2.32 (2)
Cr2-C25	2.31 (1)	2.33 (2)
-C26	2.33 (2)	2.28 (2)
-C27	2.34 (2)	2.31 (2)
-C28	2.33 (1)	2.30 (2)
-C29	2.34 (1)	2.35 (2)
C11-O1	2.34 (1)	2.35 (2)
-C12	1.50 (2)	1.50 (2)
-C13	1.53 (2)	1.55 (2)
-C14	1.52 (3)	1.54 (3)
C21-O2	1.42 (2)	1.43 (2)
-C22	1.54 (2)	1.61 (2)
-C23	1.49 (2)	1.52 (2)
-C24	1.59 (3)	1.45 (2)
C15-C16	1.41 (2)	1.33 (2)
C16-C17	1.31 (2)	1.50 (2)
C17-C18	1.45 (2)	1.52 (2)
C18-C19	1.35 (2)	1.31 (2)
C19-C15	1.45 (3)	1.39 (2)
C25-C26	1.53 (2)	1.39 (2)
C26-C27	1.41 (2)	1.32 (2)
C27-C28	1.42 (2)	1.49 (2)
C28-C29	1.36 (2)	1.39 (2)
C29-C25	1.31 (2)	1.45 (2)

^a Compare Figure 1a and Figure 1b to deduce the labeling scheme for molecule II.

number of compounds of formula Cp₂Cr₂(NO)₂X₂ are known,^{7,8} specifically for X = NMe₂, OMe, OH, and SR (R = Me and Ph), and as we show later, Cp₂Cr₂(O-*t*-Bu)₂ reacts smoothly with NO (2 equiv) to yield Cp₂Cr₂(O-*t*-Bu)₂(NO)₂. It is thus pertinent to compare the structures of the two closely related compounds Cp₂Cr₂(NO)₂(SPh)₂ and Cp₂Cr₂(O-*t*-Bu)₂. Aside from the presence in the former compound of two terminal Cr-NO moieties, the major differences arise in the central Cr₂(μ-X)₂ moiety. Cp₂Cr₂(NO)₂(SPh)₂ contains a planar Cr₂(μ-S)₂ unit and has a Cr-Cr distance of 2.950 (3) Å, whereas in Cp₂Cr₂(O-*t*-Bu)₂, there is a significantly shorter Cr-Cr distance, 2.65 (2) Å.

In the Cp₂Cr₂(XR)₂(NO)₂ (X = O, S) type compound each metal atom attains an 18-electron valence shell configuration. The ligands contribute as follows: 5 electrons from C₅H₅, 3 from XR, and 3 from NO. These 11 together with the 6 belonging to the metal atom itself make a total of 17 and the formation of a Cr-Cr single bond, although a long, weak one, then completes the effective atomic number of 18.

In Cp₂Cr₂(O-*t*-Bu)₂, however, the sum of the ligand and metal electrons (prior to Cr-Cr bonding) is only 14. The short Cr-Cr distance, 2.65 Å, indicates that a fairly strong metal-metal bond exists. The magnetism suggests that there is one unpaired electron per metal atom. These facts are most easily reconciled by postulating a Cr-Cr single bond, but we do not feel that any further analysis of the electronic structure is warranted at present.

Reactions of Cp₂Cr₂(O-*t*-Bu)₂. (a) **With Nitric Oxide.** Formation of Cp₂Cr₂(NO)₂(O-*t*-Bu)₂. Hydrocarbon solutions of Cp₂Cr₂(O-*t*-Bu)₂ react smoothly with NO (2 equiv) to give a yellow-green crystalline compound of empirical composition CpCr(NO)(O-*t*-Bu). The compound is thermally stable enough to be sublimed at 120 °C (10⁻⁴ cm Hg). A cryoscopic molecular weight determination in benzene gave 441 which compares well with that predicted for a dimer Cp₂Cr₂-

Table III. Bond Angles (deg) in Cp₂Cr₂(O-*t*-Bu)₂^a

atoms	molecule I	molecule II
Cr2-Cr1-O1	46.4 (4)	47.6 (3)
-O2	48.0 (3)	47.6 (4)
-C15	163.7 (5)	172.0 (5)
-C16	129.9 (5)	139.2 (5)
-C17	113.0 (4)	115.9 (4)
-C18	124.3 (5)	124.7 (4)
-C19	154.9 (6)	151.2 (4)
Cr1-Cr2-O1	47.0 (3)	46.9 (4)
-O2	48.3 (4)	47.4 (3)
-C25	121.5 (4)	123.7 (4)
-C26	153.4 (4)	154.1 (5)
-C27	168.5 (4)	168.1 (4)
-C28	134.4 (4)	130.9 (4)
-C29	117.1 (4)	114.9 (4)
Cr1-O1-Cr2	86.6 (4)	85.5 (4)
-C11	138 (1)	135 (1)
Cr2-O1-C11	135 (1)	139 (1)
Cr1-O2-Cr2	83.7 (4)	85.0 (4)
-C21	131 (1)	129 (1)
Cr2-O2-C21	130 (1)	130 (1)
O1-C11-C12	113 (1)	106 (1)
-C13	108 (1)	108 (1)
-C14	105 (1)	108 (1)
C12-C11-C13	105 (1)	102 (1)
-C14	102 (1)	112 (1)
C13-C12-C14	123 (2)	119 (1)
O2-C21-C22	109 (1)	107 (1)
-C23	113 (1)	109 (1)
-C24	106 (1)	110 (1)
C22-C21-C23	108 (2)	102 (1)
C22-C21-C24	100 (2)	109 (1)
C23-C21-C24	120 (2)	119 (1)
C15-C16-C17	114 (2)	112 (2)
C16-C17-C18	106 (2)	98 (1)
C17-C18-C19	108 (2)	109 (1)
C18-C19-C15	109 (2)	112 (1)
C19-C15-C16	102 (2)	108 (2)
C25-C26-C27	106 (1)	111 (2)
C26-C27-C28	106 (1)	109 (1)
C27-C28-C29	109 (1)	104 (2)
C28-C29-C15	114 (1)	109 (1)
C29-C25-C26	105 (1)	106 (1)

^a Compare Figure 1a and Figure 1b to deduce labeling scheme for molecule II.

(NO)₂(O-*t*-Bu)₂, namely 440. In the mass spectrometer the ion of highest mass was the molecular ion, Cp₂Cr₂(NO)₂(O-*t*-Bu)₂⁺, which was followed by ions formed by successive loss of NO, viz., (M - NO)⁺ and (M - 2NO)⁺. Many other Cr₂-containing ions were also observed. In the IR spectrum a strong band at 1637 cm⁻¹ is assigned to ν(NO). On the basis of these data, Cp₂Cr₂(NO)₂(O-*t*-Bu)₂ is assumed to be a member of the Cp₂Cr₂(NO)₂X₂ class of compounds discussed earlier.

(b) **With Carbon Dioxide.** Formation of Cr₂(O₂CO-*t*-Bu)₄(THF)₂. Hydrocarbon solutions of Cp₂Cr₂(O-*t*-Bu)₂ react slowly with CO₂ at moderate pressures and room temperature to produce a light red precipitate and a hydrocarbon solution of chromocene. The reaction is described by eq 3. In THF

$$2\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2 + 4\text{CO}_2 \rightarrow 2\text{Cp}_2\text{Cr} + \text{Cr}_2(\text{O}_2\text{CO}-t\text{-Bu})_4 \quad (3)$$

a similar reaction occurs and the crystalline compound Cr₂(O₂CO-*t*-Bu)₄·2THF is formed. In THF/toluene solvent the reaction is complete within ca. 2 days at room temperature; in toluene it is complete within ca. 1 week. Evidently the more polar and coordinating solvent promotes this reaction.

Solid-State Structure of Cr₂(O₂CO-*t*-Bu)₄(THF)₂. The solid compound is composed of discrete Cr₂(O₂CO-*t*-Bu)₄(THF)₂ molecules, each having a crystallographic inversion center. A perspective view of the molecule is shown in Figure 2 and the final atomic coordinates and thermal parameters are given in

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $\text{Cr}_2(\text{O}_2\text{CO-}i\text{-Bu})_4(\text{THF})_2^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.0550 (2)	0.1073 (2)	0.00687 (8)	3.47 (6)	3.30 (6)	2.74 (5)	-0.73 (8)	0.81 (5)	-0.38 (7)
O1	-0.0029 (7)	0.1319 (7)	0.0978 (3)	5.3 (3)	3.2 (3)	3.8 (3)	-2.1 (3)	1.9 (2)	-0.7 (3)
O2	-0.1028 (7)	-0.0747 (7)	0.0854 (3)	5.1 (3)	3.7 (4)	3.6 (3)	-1.0 (3)	2.1 (2)	-1.0 (3)
O3	-0.1044 (6)	0.0455 (7)	0.1789 (3)	4.5 (3)	4.0 (3)	3.3 (3)	-0.9 (3)	1.6 (2)	-0.3 (3)
O4	-0.1253 (6)	0.1878 (8)	-0.0477 (4)	2.9 (3)	4.2 (4)	5.0 (3)	-0.5 (3)	-0.1 (3)	-0.3 (3)
O5	-0.2274 (6)	-0.0153 (7)	-0.0619 (4)	3.3 (3)	3.8 (4)	4.5 (3)	-0.7 (3)	0.7 (3)	0.0 (3)
O6	-0.3370 (7)	0.1790 (8)	-0.1078 (4)	3.4 (3)	5.7 (4)	6.3 (4)	0.1 (4)	-0.9 (3)	0.8 (4)
O7	0.1613 (8)	0.3124 (8)	0.0212 (4)	7.7 (4)	5.3 (4)	5.1 (4)	-3.2 (4)	1.6 (3)	0.0 (4)
C1	-0.0685 (10)	0.037 (1)	0.1168 (5)	4.3 (5)	3.7 (5)	2.6 (4)	0.8 (5)	0.9 (4)	-0.2 (4)
C2	-0.0808 (11)	0.173 (1)	0.2236 (5)	5.7 (5)	4.4 (6)	3.8 (4)	-0.7 (5)	2.6 (4)	-1.9 (4)
C3	0.0794 (10)	0.195 (1)	0.2504 (6)	3.6 (5)	6.3 (6)	5.3 (6)	-1.8 (5)	0.4 (5)	-2.2 (6)
C4	-0.1363 (12)	0.126 (1)	0.2869 (6)	7.1 (6)	8.0 (8)	4.9 (5)	-0.8 (7)	4.1 (4)	-1.5 (6)
C5	-0.1570 (13)	0.292 (1)	0.1829 (7)	6.8 (7)	4.4 (6)	7.1 (7)	1.7 (6)	1.1 (6)	0.9 (6)
C6	-0.2249 (9)	0.115 (1)	-0.0712 (5)	1.9 (4)	5.9 (6)	2.7 (4)	-0.5 (5)	-0.3 (3)	-0.6 (5)
C7	-0.4635 (11)	0.104 (1)	-0.1449 (7)	3.0 (5)	7.6 (8)	7.2 (7)	0.1 (7)	-1.2 (5)	2.1 (7)
C8	-0.5246 (12)	0.029 (2)	-0.0936 (9)	3.5 (6)	15 (1)	12 (1)	-1.2 (8)	2.5 (6)	4.3 (9)
C9	-0.4264 (15)	0.010 (2)	-0.2012 (8)	7.7 (8)	12 (1)	6.1 (7)	-1.0 (9)	0.0 (7)	-3.8 (8)
C10	-0.5566 (14)	0.224 (2)	-0.1799 (10)	4.7 (7)	12 (1)	13 (1)	1.9 (9)	-4.8 (7)	2 (1)
C11	0.2520 (19)	0.358 (2)	0.0861 (8)	16 (1)	12 (1)	5.6 (7)	-7.7 (9)	1.3 (8)	-2.1 (8)
C12	0.3418 (18)	0.461 (2)	0.0688 (10)	12 (1)	16 (1)	12 (1)	-9.5 (9)	-3 (1)	4 (1)
C13	0.2878 (18)	0.493 (2)	-0.0067 (9)	14 (1)	13 (1)	7.8 (8)	-8.6 (8)	2.3 (8)	0.3 (9)
C14	0.1771 (18)	0.397 (2)	-0.0333 (8)	14 (1)	10.0 (9)	7.8 (8)	-7.1 (8)	-0.5 (8)	3.2 (8)

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$.

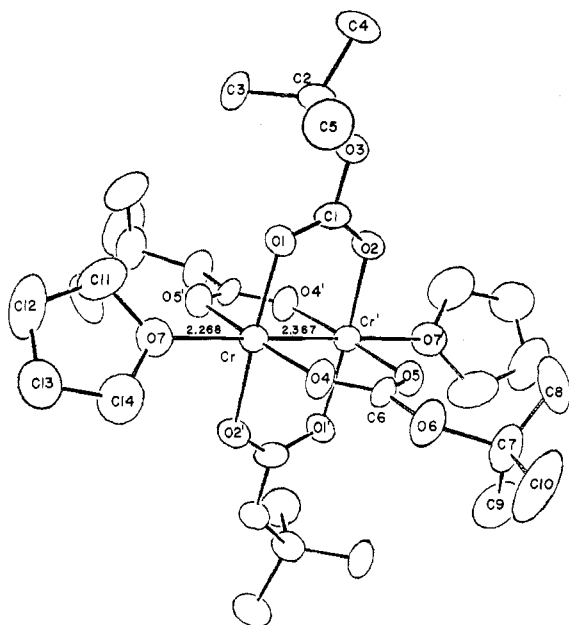
**Figure 2.** View of the $\text{Cr}_2(\text{O}_2\text{CO-}i\text{-Bu})_4(\text{THF})_2$ molecule using 40% probability ellipsoids and showing the atom labeling scheme.

Table IV. Bond distances and angles are given in Tables V and VI, respectively. The structure is similar to those seen for dichromium tetracarboxylate compounds $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ of which numerous examples have recently been examined crystallographically.^{9,10} The $\text{Cr}_2(\text{O}_2\text{COC})$ moieties are planar and the planes defined by the two unique $\text{Cr}_2(\text{O}_2\text{COC})$ moieties make a dihedral angle of 88° . The tetrahydrofuran molecules are coordinated axially with $\text{Cr}'\text{-Cr-O7} = 179.4 (2)^\circ$. The Cr-Cr distance of $2.367 (3) \text{ \AA}$ and axial Cr-O bond length, $2.268 (7) \text{ \AA}$, are consistent with those observed for many $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds.^{9,10}

(c) **With Other Unsaturated Molecules.** An exploratory survey of the reactivity of $\text{Cp}_2\text{Cr}_2(\text{O-}i\text{-Bu})_2$ toward small unsaturated molecules was undertaken. In separate experiments hydrocarbon solutions of $\text{Cp}_2\text{Cr}_2(\text{O-}i\text{-Bu})_2$ were exposed to each of the following at a few atmospheres pressure and room temperature: methylacetylene, diethylacetylene, hexafluoro-2-butyne, allene, carbon monoxide, and nitrous oxide.

Table V. Bond Distances (Å) in $\text{Cr}_2(\text{O}_2\text{CO-}i\text{-Bu})_4(\text{THF})_2$

Cr-Cr'	2.367 (3)	C6-O4	1.217 (9)
-O1	2.014 (6)	-O5	1.301 (11)
-O2'	1.999 (5)	-O6	1.325 (10)
-O4	2.010 (6)	C7-O6	1.49 (1)
-O5'	2.002 (6)	-C8	1.49 (2)
-O7	2.268 (7)	-C9	1.55 (2)
C1-O1	1.253 (10)	-C10	1.55 (2)
-O2	1.263 (10)	C11-O7	1.43 (1)
-O3	1.348 (9)	-C12	1.45 (2)
C2-O3	1.51 (1)	C12-C13	1.47 (2)
-C3	1.57 (1)	C13-C14	1.45 (2)
-C4	1.55 (1)	C14-O7	1.39 (1)
-C5	1.51 (1)		

Table VI. Bond Angles (deg) in $\text{Cr}_2(\text{O}_2\text{CO-}i\text{-Bu})_4(\text{THF})_2$

Cr'-Cr-O1	88.7 (2)	O3-C2-C5	110.9 (7)
-O2'	88.0 (2)	C3-C2-C4	108.7 (8)
-O4	87.9 (2)	-C5	113.9 (8)
-O5'	88.2 (2)	C4-C2-C5	114.5 (8)
-O7	179.4 (2)	Cr-O4-C6	120.4 (7)
O1-Cr-O2'	176.5 (2)	Cr'-O5-C6	118.5 (6)
-O4	89.8 (2)	O4-C6-O5	124.8 (9)
-O5'	89.2 (2)	-O6	115 (1)
-O7	90.9 (2)	O5-C6-O6	120.0 (8)
O2'-Cr-O4	88.6 (2)	C6-O6-C7	121.8 (8)
-O5'	92.1 (2)	O6-C7-C8	111.3 (9)
-O7	92.4 (3)	-C9	108.2 (8)
O4-Cr-O5'	176.0 (3)	-C10	100.3 (9)
-O7	92.5 (3)	C8-C7-C9	113 (1)
O5'-Cr-O7	91.4 (3)	-C10	112 (1)
Cr-O1-C1	117.4 (5)	C9-C7-C10	112 (1)
Cr'-O2-C1	118.6 (6)	Cr-O7-C11	124.2 (7)
O1-C1-O2	127.3 (8)	-C14	125.5 (7)
-O3	119.8 (9)	C11-O7-C14	108.5 (9)
O2-C1-O3	112.9 (8)	O7-C11-C12	108 (1)
C1-O3-C2	122.1 (7)	C11-C12-C13	107 (1)
O3-C2-C3	107.6 (7)	C12-C13-C14	106 (1)
-C4	100.1 (7)	O7-C14-C13	110 (1)

No reaction was observed for either diethylacetylene or allene; methylacetylene and nitrous oxide reacted but no pure product was characterized. With carbon monoxide a nonvolatile, hydrocarbon-insoluble compound of empirical formula $\text{CpCr}(\text{O-}i\text{-Bu})(\text{CO})_2$ was obtained. This compound showed several infrared bands in the carbonyl stretching region. With $\text{CF}_3\text{C}\equiv\text{CCF}_3$ a smooth reaction occurred yielding a purple, thermally stable and sublimable (140°C (10^{-4} cm Hg))

crystalline compound, $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$. This compound is formulated as a 1:1 adduct on the basis of (1) analytical data, (2) a cryoscopic molecular weight determination, and (3) its mass spectrum. The last shows a molecular ion $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2(\text{C}_4\text{F}_6)^+$ followed by loss of C_4F_6 to give the peak $\text{Cp}_2\text{Cr}_2(\text{O}-t\text{-Bu})_2^+$. From this we conclude that hexafluoro-2-butyne has not irreversibly attacked the Cp ring or reacted with the *tert*-butoxy ligand. However, there is no band in the infrared spectrum readily assignable to $\nu(\text{C}\equiv\text{C})$, and since the compound is paramagnetic and does not yield to NMR investigations, the nature of the coordination of the acetylene is unknown. Crystals suitable for X-ray studies have not yet been obtained. Full spectroscopic data of this interesting 1:1 acetylene adduct are given in the Experimental Section.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-O}-t\text{-Bu})_2$, 68108-73-6; $\text{Cr}_2(\text{O}_2\text{CO}-t\text{-Bu})_2(\text{THF})_2$, 68108-74-7; $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{O}-t\text{-Bu})_2(\text{NO})_2$, 68108-75-8; hexafluoro-2-butyne, 692-50-2; $\text{C}_5\text{H}_5\text{Cr}(\text{O}-t\text{-Bu})(\text{CO})_2$, 68108-76-9; chromocene, 1271-24-5.

Supplementary Material Available: Tables of structure factors (15 pages). See any current masthead page for ordering information.

References and Notes

- (1) (a) Princeton University. (b) Texas A&M University.
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Oxygen-Carrying Cobalt Complexes. 9.

Preparation and Crystal Structure of the Dioxygen Adduct of

Aquo[*N,N'*-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideneiminato)]cobalt(II)¹

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The dioxygen adduct of aquo[*N,N'*-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideneiminato)]cobalt(II) ($(\text{H}_2\text{O})\text{-Co}(\text{3-OMe-Saltmen})$) has been prepared and crystallized as a dimethoxyethane solvate. The material crystallizes in a monoclinic cell, space group $P2_1/c$, with $a = 10.918$ (1) Å, $b = 20.035$ (1) Å, $c = 13.442$ (1) Å and $\beta = 110.21$ (1)°. There are four formula units of $\text{Co}_2\text{O}_2\text{N}_2\text{C}_{22}\text{H}_{26}\text{O}_2\cdot\text{H}_2\text{O}\cdot\text{C}_4\text{H}_{10}\text{O}_2$ in the cell. Intensity measurements were made on an automatic diffractometer using a θ - 2θ scan technique; 3750 independent reflections were used in a least-squares refinement which led to a final R index of 0.095. The $\text{Co}(\text{3-OMe-Saltman})$ portion of the molecule has normal geometry. The dioxygen molecule is disordered between two positions, with an average Co-O distance of 1.88 (1) Å and an average O-O distance of 1.25 (2) Å. The axial base trans to the dioxygen group is a water molecule 2.048 (4) Å from the cobalt atom.

In recent years, many studies of metal complexes with dioxygen as one ligand have been reported. The impetus behind these studies is, of course, understanding the binding between oxygen and transition metals in the proteins involved in oxygen transport in living beings. One of the first questions, that of the geometry of the dioxygen group and the iron atom in oxyhemoglobin, has been settled by X-ray studies of the iron picket fence porphyrin² and of several cobalt-dioxygen complexes.³ The consistent picture is the one predicted by Pauling in 1949,⁴ with a "bent" metal-O-O geometry. What is not yet clear or understood is the detailed description of the metal-oxygen binding. From a simple molecular orbital view, the metal-dioxygen bond is the result of the transfer of some electron density from the metal to antibonding orbitals on the oxygen. If this is the case, then the O-O bond length should depend on the availability of electrons at the metal atom, which in turn should depend on the other ligands attached to the metal. By studying the influence of other ligands on the O-O distance or the M-O-O geometry, it should be possible to explain in detail the electronic state of the bound dioxygen.

Some recent theoretical studies⁵ have suggested, on the other hand, that the bonding of O_2 to Fe in oxyhemoglobin and oxymyoglobin is essentially similar to the bonding of O_2 to O in ozone. This description implies that the O-O bond is a combination of a normal σ bond and a three-center, four-electron π bond. Such a description is said to explain many

of the experimental observations regarding oxyhemoglobin; it also accounts for the ~ 1.3 Å O-O bond distance observed in model compounds. The π bond is formed from electrons in the d_{xz} orbital of the metal atom; the electron density in this orbital can be influenced by groups on the in-plane ligands or by axial groups. Thus, in order to obtain experimental evidence which can support or refute this hypothesis, or the others which can be tested, it is necessary to obtain experimental information regarding the molecular geometries of oxygen adducts of metal ions with various ligand systems and axial bases. This paper reports the crystal and molecular structure of a dioxygen adduct of [*N,N'*-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideneiminato)]cobalt(II) ($\text{Co}(\text{3-OMe-Saltmen})$; Saltmen = Salen with tetramethyl substitution on the en bridge), a reversibly oxygenated complex with a ring substituent on the in-plane ligand (3-methoxy) which has not been studied before and with a previously unknown axial base, a water molecule.

Experimental Section

Materials. 2,3-Dimethyl-2,3-dinitrobutane was purchased from Aldrich Chemical Co., 1,2-dimethoxyethane from MCB, pyridine from Mallinckrodt, and 2-hydroxy-3-methoxybenzaldehyde from California Corporation for Biochemical Research.

Preparation of the Schiff Base (3-OMe-Saltmen). 2,3-Diamino-2,3-dimethylbutane was prepared according to published procedure.⁶ A 3.438-g sample of 2-hydroxy-3-methoxybenzaldehyde