dium orbitals by $\pi$ *donation* of electron density from the sulfur atoms to palladium. Thus, the sulfur donor ligands may stabilize palladium alkyls because of the formation of strong S–Pd bonds and the donation of electron density to empty palladium orbitals blocking the $\beta$-elimination process.

The crystal structures of the isomers 1 and 2 offer a unique opportunity to compare the bonding of a linear and branched alkyl ligand in a metal complex in which there is *minimal steric influences from the ancillary ligand.* The most important conclusion that can be made from the two structures is that they are very similar; changing from a primary to a secondary alkyl ligand has only a small structural effect. It is known that primary alkyls are generally much easier to prepare in most transition-metal systems.[1] For the $(R_2NCS_2)M(PEt_3)(alkyl)$ (M = Pd, Pt) complexes, the ease of preparation and thermal stability of the primary and secondary isomers are very similar. Thus, we conclude that in other systems the primary alkyl isomers are generally easier to prepare because steric crowding from the ancillary ligands destabilizes secondary alkylmetal complexes.

Another interesting feature of the structures is the greater trans influence of the isopropyl ligand compared to the *n*-propyl ligand. For comparison, the alkylmetal complexes studied most extensively by crystallographic means are the cobaloximes, analogues of the $B_{12}$ coenzyme.[19] Although this octahedral system has important steric interactions that influence the alkyl ligands, parallel to our observations, it has been found that the Co–X bond trans to the alkyl is longer for an isopropyl than an analogous ethyl derivative.[19]

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**Supplementary Material Available:** Tables of positional parameters of H atoms and anisotropic thermal parameters (6 pages); listings of structure factor amplitudes (44 pages). Ordering information is given on any current masthead page.

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# Organometallic Oxides: Preparation and Properties of the Tetrahedral ($T_d$) Cubane $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ and Comparison with the $D_2$ $[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4$ and $D_{2d}$ $[(\eta\text{-}C_5H_4CH_3)Cr(\mu_3\text{-}O)]_4$

Frank Bottomley,* Jinhua Chen, and Sarajane M. MacIntosh

*Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*

Robert C. Thompson

*Department of Chemistry, University of British Columbia, 2036 Main Mall,*
*Vancouver, British Columbia, Canada V6T 1Y6*

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The cubane $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3) was prepared by the reaction between $(\eta\text{-}C_5(CH_3)_5)_2Cr$ (4) and $N_2O$ (1:1 molar ratio) in toluene at 80 °C. The structures of 3 and 4 have been determined by X-ray diffraction. 3: $M_r$ = 813.0, triclinic, $P\bar{1}$, $a$ = 10.876 (2) Å, $b$ = 10.923 (2) Å, $c$ = 18.105 (2) Å, $\alpha$ = 83.75 (1)°, $\beta$ = 83.89 (1)°, $\gamma$ = 66.86 (1)°, $Z$ = 2, $R$ = 0.060, $R_w$ = 0.080 for 4121 observed reflections and 463 refined parameters. 4: $M_r$ = 322.45, orthorhombic, *Ccmm*, $a$ = 8.6857 (5) Å, $b$ = 14.7842 (8) Å, $c$ = 29.2031 (15) Å, $Z$ = 8, $R$ = 0.079, $R_w$ = 0.092 for 816 observed reflections and 100 parameters. 3 has $T_d$ symmetry, the six Cr–Cr distances averaging 2.834 (2), and the Cr–O distances, 1.945 (5) Å. The Cr–O–Cr angles average 93.5 (2); the O–Cr–O angles, 86.4 (2)°. 3 is antiferromagnetic, the magnetic moment increasing from 1.10 at 4.5 to 1.94 $\mu_B$ at 84.5 K; at 295 K the moment was 3.74 $\mu_B$. The physical and chemical properties of 3 are compared to those of $[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4$ (1), which has $D_2$ symmetry, and to $[(\eta\text{-}C_5H_4CH_3)Cr(\mu_3\text{-}O)]_4$, which has $D_{2d}$ symmetry. It is concluded that the $\eta\text{-}C_5R_5$ ring does not influence the $[Cr(\mu_3\text{-}O)]_4$ core. Whereas 1 lost all $\eta\text{-}C_5H_5$ ligands rapidly on treatment with $O_2$, 3 was essentially inert to it.

## Introduction

In previous papers we have discussed the preparation[1,2] and physical properties[3] of the cubane $[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4$ (1). This intriguing cluster, which was the first cubane prepared (in 1960), though it was not then recognized as such,[4] has a markedly distorted ($D_2$) structure, with three pairs of Cr–Cr distances, the pairs averaging 2.8960 (5),

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**Table I. Distances (Å) and Angles (deg) in $[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4$ (1), $[(\eta\text{-}C_5H_4CH_3)Cr(\mu_3\text{-}O)]_4$ (2), and $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3)**

| | 1 | 2 | 3 |
|---|---|---|---|
| Cr–Cr | 2.896 (1, 3)[a] | 2.896 (3) | 2.834 (2, 3, 6) |
| | 2.823 (1, 13) | 2.759 (3) | |
| | 2.706 (1, 5) | | |
| Cr–O | 1.936 (2, 6, 14) | 1.947 (8, 8, 13) | 1.945 (5, 10, 25) |
| Cr–C | 2.259 (3, 10, 20) | 2.28 (1, 2, 3) | 2.270 (8, 12, 22)[b] |
| Cr–Cp | 1.918 (2, 5, 10) | 1.923 (1) | 1.932 (8, 9, 13) |
| O–Cr–O | 83.24 (7, 14, 18) | 83.9 (3) | 86.36 (19, 51, 93) |
| | 86.30 (7, 27, 35) | 89.3 (3, 2, 2) | |
| | 90.15 (7, 27, 49) | | |
| Cr–O–Cr | 88.79 (7, 34, 68) | 90.3 (3, 2, 2) | 93.52 (20, 60, 124) |
| | 93.65 (7, 29, 42) | 95.8 (3) | |
| | 96.64 (7, 41, 60) | | |
| $C_5$–$C_{ring}$[c] | 3.36 | 3.50 | 3.59 |

[a] The first figure is the esd, the second, the average deviation from the mean, and the third, the maximum deviation from the mean. [b] The Cr–C average for **3** does not include the disordered ring attached to Cr(2). [c] Intermolecular contact.

2.8234 (5), and 2.7059 (6) Å (see Table I). The cluster **1** is antiferromagnetic, its magnetic moment increasing from zero at <50 K to 3.85 $\mu_B$ at 500 K. This antiferromagnetic behavior is in marked contrast to the $[(\eta\text{-}C_5R_5)M(\mu_3\text{-}S)]_4^{n+}$ cubanes (R = H and/or organic group; M = Ti,[5] V,[5,6] Cr,[7,8] Fe,[9,10] Co,[11] Mo,[12-14] Ru;[15] $n = +2$ to $-2$ for M = Fe[16,17]), which, with the exception of the V derivative for which $\mu_{eff} = 2.67\ \mu_B$,[5] are low-spin, at least up to 300 K. We originally assumed that the distortion of **1** from $T_d$ symmetry was related to the antiferromagnetism.[2,18] Two pieces of evidence suggest that this assumption is wrong. First, the distortion remains the same, in magnitude and direction, over the temperature range 100–295 K while the magnetic moment changes by 2.15 $\mu_B$ over this temperature range.[3] Second, $[(\eta\text{-}C_5H_4CH_3)Cr(\mu_3\text{-}O)]_4$ (**2**) has $D_{2d}$ symmetry (Cr–Cr distances of 2.896 (3) (×2) and 2.759 (3) (×4) Å, Table I) but is also antiferromagnetic, the magnetic moment varying from 0.60 $\mu_B$ at 77 K to 2.64 $\mu_B$ at 296 K.[19] The antiferromagnetism of **1** and **2** is due to the partial occupation of 12 cluster orbitals, which are close in energy, by 12 electrons.[3,12] The closeness of these levels appears to be independent of the $\eta$-$C_5R_5$ ligand, though their detailed ordering must change because of the change in symmetry on going from **1** to **2**. The distortion, on the other hand, appears to be dependent on the $\eta$-$C_5R_5$ ligand. This is different from the $[(\eta\text{-}C_5R_5)M(\mu_3\text{-}S)]_4$ cubanes, which are only distorted from $T_d$ symmetry when the number of cluster electrons is greater than 12; the distortions are then larger than for $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$ and are not dependent on the $\eta$-$C_5R_5$ ring but are dependent on the number of electrons.[12,17]

In order to explore the relationship between the $\eta$-$C_5R_5$ ligand and the distortion to the cubane we wished to prepare $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (**3**). This cubane appeared unlikely to exist, since the $\eta$-$C_5H_5$ rings in **1** are already rather crowded sterically. We were encouraged by the recent preparation of the admantane-like clusters $[(\eta\text{-}C_5(CH_3)_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti,[20,21] V[22]) and $\{[(\eta\text{-}C_5(CH_3)_5)Cr]_4(\mu_2\text{-}OH)_6\}^{2+}$.[23] The M–M distances in the titanium and vanadium compounds (3.229 (3) and 3.003 (3) Å, respectively) are only 0.3–0.5 Å longer than was to be expected for **3**. We report here the preparation of **3** by a method similar to that used for **1** (oxidation of $(\eta\text{-}C_5H_5)_2Cr$ with $N_2O$) and a detailed description of its physical properties, which are compared to those of **1** and **2**.

## Results and Discussion

**Preparation of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3).** A toluene solution of $(\eta\text{-}C_5(CH_3)_4)_2Cr$ (**4**) turned from deep red to deep green on treatment with $N_2O$ (1:2 molar ratio) for 7 days at 20 °C. Workup was complicated by the presence of the involatile oil $(C_5(CH_3)_5)_2$, produced according to eq 1. This prevented purification of **3** by sublimation. The

$$4(\eta\text{-}C_5(CH_3)_5)_2Cr + 4N_2O \rightarrow [(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4 + 4N_2 + 2(C_5(CH_3)_5)_2 \quad (1)$$

extraction/evaporation technique described in the Experimental Section yielded pure, crystalline **3** in 39% yield. Longer reaction times lead to formation of $[(\eta\text{-}C_5(CH_3)_5)Cr(O)(\mu\text{-}O)]_2$,[24] as well as **3**. We suspect that this product arises from slow infusion of $O_2$, since oxidation of **4** with $O_2$ gave $[(\eta\text{-}C_5(CH_3)_5)Cr(O)(\mu\text{-}O)]_2$ (see below).

**Chemical and Physical Properties of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3).** The cluster **3** is turquoise and sublimable at 300 °C in vacuo. It is considerably less air sensitive and also considerably less soluble in hexane or toluene than **1**. The somewhat surprisingly low solubility in hexane or toluene led us to investigate other solvents; **3** is soluble in hydrocarbon solvents when the solvent molecules are large, e.g. decahydronaphthalene and $(C_5(CH_3)_5)_2$ (accounting for the difficulty in the purification of crude **3**), as well as in $CHCl_3$ and $CCl_4$. We believe that the size of **1**, which can be regarded as a sphere of radius 5.5 Å, requires that hydrocarbon solvent molecules also be large to avoid disruption of the solvent structure.

The infrared spectrum of **3** showed an intense absorption band at 550 $cm^{-1}$ with a shoulder at 525 $cm^{-1}$. This band is assigned to the antitranslation vibration mode of the $[Cr(\mu_3\text{-}O)]_4$ core; its frequency is less than that of **1** (555

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cm$^{-1}$[3]) or 2 (590 cm$^{-1}$[19]). If the $\eta$-$C_5R_5$ ligand had no affect on the $[Cr(\mu_3\text{-}O)]_4$ core, then the frequencies of the antitranslation vibration of **1**–**3** would be the same. If, on the other hand, the $\eta$-$C_5R_5$ was strongly attached to the $[Cr(\mu_3\text{-}O)]_4$ core, simple mass effects suggest that the order of the frequencies would be **1** > **2** > **3**. The observed order is **2** > **1** > **3**. The significance of this is not clear.

The mass spectrum (in the FAB mode) of **3** showed, as its highest peak, *m/e* 813 [$(M + H)^+$], together with all peaks of the type $(C_5(CH_3)_5)_nCr_4O_4^+$ ($n$ = 3–0), as well as all peaks of type $(C_5(CH_3)_5)_nCr_4O_3$ ($n$ = 3–0). Spectra in the EI mode were similar but with much less fragmentation. The loss of $C_5(CH_3)_5$ from **3** was much less evident than the loss of $C_5H_5$ from **1** under the same conditions. This suggests that loss of the $\eta$-$C_5R_5$ ligand from $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$ is determined by electronic rather than steric factors.

Since it was not clear why either **1** or **3** should be sensitive to air (being formally derivatives of Cr(III)), their reaction with $O_2$ and $H_2O$ was investigated in detail. **1** was extremely sensitive to $O_2$, turning from blue to brown immediately, either in solution or in the solid state. The reaction between **1** and $H_2O$ was very much slower, there being no immediate change when **1** was exposed to equimolar quantities of $H_2O$. However, water converted blue **1** to the same brown material as was produced by $O_2$ over a period of several hours. The brown material was insoluble in all solvents except DMSO, and is assumed to be polymeric. Microanalysis gave an approximate formula of $[Cr_2O_3(THF)_6]_n$. Magnetic measurements clearly established that the material contained Cr(III). Spectroscopic evidence (infrared and NMR) suggested that the brown material contained no $C_5H_5$ ligands. This was confirmed by reaction with $SOCl_2$ which gave a high yield of the known compound $CrCl_3(THF)_3$.[25] Thus oxidation of **1** with $O_2$ resulted in complete loss of the $\eta$-$C_5H_5$ rings, while the metal remained in the same oxidation state. The probable equation for this reaction is (2). In this respect

$$[(\eta\text{-}C_5H_5)Cr(\mu_3\text{-}O)]_4 + O_2 + 12THF \rightarrow 2Cr_2O_3(THF)_6 + 2(C_5H_5)_2 \quad (2)$$

**1** behaves like ionic cyclopentadienyl derivatives such as $(C_5H_5)M$ (M = Li, Na, K), which are very readily oxidized by $O_2$, although it is obvious that the $C_5H_5$ ring, not the metal, undergoes oxidation. The precursor to **1**, $(\eta\text{-}C_5H_5)_2Cr$, reacted with $O_2$ to give a low yield of **1**, as originally reported by Fischer, Ulm, and Fritz.[4] However, the major product was $[Cr_2O_3(thf)_6]_n$. Thus $(\eta\text{-}C_5H_5)_2Cr$ reacted as both a covalent and an ionic cyclopentadienyl derivative.

In contrast to the reaction between **1** and $O_2$, **3** was oxidized very slowly indeed by $O_2$. Because the reaction was so slow, no product could be identified. Oxidation of **4** by $O_2$ proceeded rapidly and smoothly according to eq 3. The yield of $[(\eta\text{-}C_5(CH_3)_5)Cr(O)(\mu\text{-}O)]_2$ was approximately 17% after purification. The reaction, although a one-pot synthesis, is not an improved synthesis of $[(\eta\text{-}C_5(CH_3)_5)Cr(O)(\mu\text{-}O)]_2$ (compared to the reaction between $(\eta\text{-}C_5(CH_3)_5)Cr(CO)_2(NO)$ and $O_2$ described by Herberhold and co-workers[24]) because repeated chromatography was necessary to remove oily $(C_5(CH_3)_5)_2$ from the product. Reaction 3 is however remarkable since a Cr(II) derivative is oxidized to Cr(V) in a single step. It is clear that **3** cannot be an intermediate in reaction 3 because of the extremely slow rate of the reaction between **3** and $O_2$.

$$2(\eta\text{-}C_5(CH_3)_5)_2Cr + O_2 \rightarrow [(\eta\text{-}C_5(CH_3)_5)Cr(O)(\mu\text{-}O)]_2 + (C_5(CH_3)_5)_2 \quad (3)$$

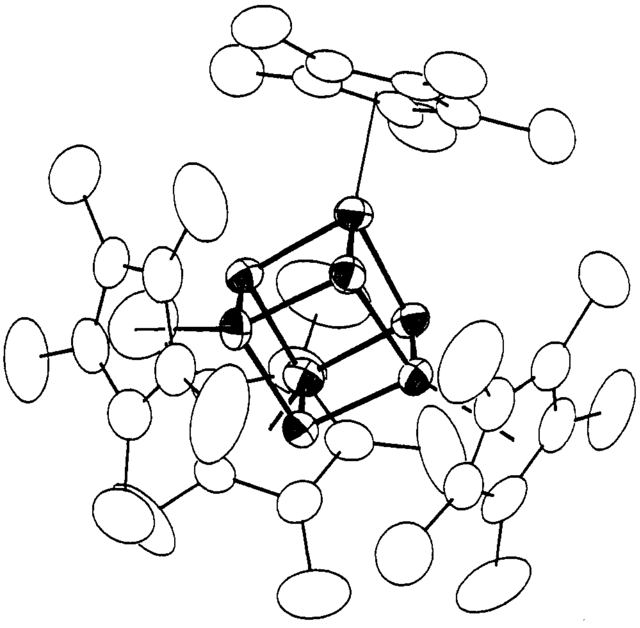

**Figure 1.** ORTEP plot of the molecular structure of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu\text{-}O)]_4$ (**3**). Only one of the disordered $C_5(CH_3)_5$ rings attached to Cr(2) is shown, and hydrogen atoms are omitted for clarity.

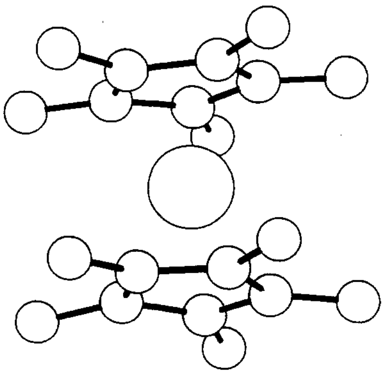

**Figure 2.** Structure of $(\eta\text{-}C_5(CH_3)_5)_2Cr$. Only one of the several disordered molecules is shown, and hydrogen atoms are omitted for clarity.

**Table II. Important Distances (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| Cr(1)–Cr(2) | 2.828 (2) | O(2)–Cr(1)–O(3) | 87.2 (2) |
| Cr(1)–Cr(3) | 2.830 (2) | O(2)–Cr(1)–O(4) | 86.9 (2) |
| Cr(1)–Cr(4) | 2.840 (2) | O(3)–Cr(1)–O(4) | 86.7 (2) |
| Cr(2)–Cr(3) | 2.834 (2) | O(1)–Cr(2)–O(2) | 87.0 (2) |
| Cr(2)–Cr(4) | 2.837 (2) | O(1)–Cr(2)–O(4) | 86.6 (2) |
| Cr(3)–Cr(4) | 2.832 (2) | O(2)–Cr(2)–O(4) | 86.7 (2) |
| Cr(1)–O(2) | 1.944 (5) | O(1)–Cr(3)–O(2) | 85.9 (2) |
| Cr(1)–O(3) | 1.920 (5) | O(1)–Cr(3)–O(3) | 85.8 (2) |
| Cr(1)–O(4) | 1.945 (5) | O(2)–Cr(3)–O(3) | 85.8 (2) |
| Cr(2)–O(1) | 1.925 (5) | O(1)–Cr(4)–O(3) | 86.5 (2) |
| Cr(2)–O(2) | 1.949 (5) | O(1)–Cr(4)–O(4) | 85.7 (2) |
| Cr(2)–O(4) | 1.948 (5) | O(3)–Cr(4)–O(4) | 85.4 (2) |
| Cr(3)–O(1) | 1.947 (5) | Cr(2)–O(1)–Cr(3) | 94.1 (2) |
| Cr(3)–O(2) | 1.966 (5) | Cr(2)–O(1)–Cr(4) | 94.6 (2) |
| Cr(3)–O(3) | 1.950 (5) | Cr(3)–O(1)–Cr(4) | 93.7 (2) |
| Cr(4)–O(1) | 1.934 (5) | Cr(1)–O(2)–Cr(2) | 93.1 (2) |
| Cr(4)–O(3) | 1.940 (5) | Cr(1)–I(2)–Cr(3) | 92.7 (2) |
| Cr(4)–O(4) | 1.970 (5) | Cr(1)–O(3)–Cr(3) | 94.0 (2) |
| Cr(1)–Cp(1) | 1.919 (8) | Cr(1)–O(3)–Cr(4) | 94.8 (2) |
| Cr(2)–Cp(2) | 1.923 | Cr(3)–O(3)–Cr(4) | 93.5 (2) |
| Cr(3)–Cp(3) | 1.936 (8) | Cr(1)–O(4)–Cr(2) | 93.2 (2) |
| Cr(4)–Cp(4) | 1.943 (8) | Cr(2)–O(4)–Cr(4) | 93.0 (2) |
| | | Cr(2)–O(4)–Cr(4) | 92.8 (2) |

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**Table III. Comparison of the Cell Dimensions and Metal–Ring Distances in [(η-$C_5(CH_3)_5$)Cr($\mu_3$-O)]$_4$ (3) and [(η-$C_5(CH_3)_5$)M]$_4$($\mu_3$-O)$_6$**

| | 3 | M = V[a] | M = Ti[b] |
|---|---|---|---|
| *a*, Å | 10.876 (2) | 11.077 (5) | 11.278 (3) |
| *b*, Å | 10.923 (2) | 11.113 (4) | 11.355 (3) |
| *c*, Å | 18.105 (2) | 18.394 (10) | 18.694 (4) |
| α, deg | 83.75 (1) | 83.59 (4) | 83.13 (2) |
| β, deg | 83.89 (1) | 83.73 (4) | 83.18 (2) |
| γ, deg | 66.86 (1) | 66.62 (4) | 66.12 (2) |
| *V*, $Å^3$ | 1961.3 (5) | 2060 (2) | 2167 (1) |
| M–centroid, Å | 1.932 (8) | 2.023 (10) | 1.978 |

[a] Reference 22. [b] Transformed from the cell given in ref 20.

**Crystal and Molecular Structure of [(η-$C_5(CH_3)_5$)-Cr(μ-O)]$_4$ (3).** An ORTEP[26] plot of the structure of 3, as determined by X-ray diffraction, is shown in Figure 1, and important distances and angles are given in Table II. We were pleasantly surprised to find that four η-$C_5(CH_3)_5$ rings could indeed be packed around a core having a metal–metal distance of only 2.83 Å. In {[(η-$C_5(CH_3)_5$)Cr]$_4$(μ-OH)$_6$}$^{2+}$ the Cr–Cr distance is 3.669 (2) Å;[23] in [(η-$C_5(CH_3)_5$)M]$_4$($\mu_2$-O)$_6$ it is 3.229 (7) Å for M = Ti[20] and 3.003 (3) Å for M = V.[22] The closest intramolecular C–C distances between $CH_3$ groups on adjacent rings in 3 is 3.59 Å. There are a number of $CH_3$–C(ring) distances of approximately 3.65 Å, which is also the value of many intermolecular C–C distances of both the $CH_3$–$CH_3$ and $CH_3$–C(ring) type. No attempt was made to assess the H–H contacts, and several short distances involving the disordered ring 2 were ignored. The closest intramolecular C(ring)–C(ring) distance in 1 is 3.36 Å,[3] and in 2 it is 3.50 Å[19] (see Table I for a comparison of the important parameters of 1–3).

The Cr–$C_5$ ring centroid distance in 3 is 1.932 (8, 9, 13) Å (ring 2 being ignored). The same distance is 1.918 (2, 5, 10) Å in 1[3] and 1.923 (1) Å in 2.[19] While there is a trend to longer distance as the steric bulk of the ring increases, it is of marginal significance and only 0.014 Å in total magnitude. It was of interest to determine whether the lack of change in the Cr–C distances in 1–3 was peculiar to these clusters or more general. To this end we determined the structure of (η-$C_5(CH_3)_5$)$_2$Cr (4). As described in the Experimental Section and discussed below, 4 is so disordered in the crystal that accurate details of the structure cannot be obtained. However the average Cr–C ring centroid distance is 1.797 Å;[27,28] in (η-$C_5H_5$)$_2$Cr it is 1.798 (4) Å, as determined in the gas phase by electron diffraction.[29]

In assessing the significance of the Cr–C ring distances, the role of steric factors, and also the affect of these parameters on the [Cr($\mu_3$-O)]$_4$ core, it is instructive to compare 3 to [(η-$C_5(CH_3)_5$)M]$_4$($\mu_2$-O)$_6$ (M = Ti,[20] V[22]). This is done in Table III. The remarkable similarity is obvious. The differences in the cell dimensions are solely attributable to the different covalent radii of Cr (1.25 Å), V (1.27 Å), and Ti (1.32 Å[30]). It is concluded from the data in Table III that the cell dimensions and volumes of the clusters are determined by the η-$C_5(CH_3)_5$M units, and the nature of the cores ([Cr($\mu_3$-O)]$_4$ versus [M$_4$($\mu_2$-O)$_6$]) plays no role. This conclusion is supported by the parameters for the (η-$C_5(CH_3)_5$)$_2$M compounds that are given in Table IV. It is again seen that the M(η-$C_5(CH_3)_5$) unit determines the cell dimensions and volume.

**Table IV. Comparison of the Cell Dimensions and Metal–Ring Distances in (η-$C_5(CH_3)_5$)$_2$M Compounds**

| | (η-$C_5(CH_3)_5$)$_2$V[a] | (η-$C_5(CH_3)_5$)$_2$Cr |
|---|---|---|
| *a*, Å | 8.660 (4) | 8.6857 (5) |
| *b*, Å | 15.049 (6) | 14.7842 (8) |
| *c*, Å | 29.663 (10) | 29.2031 (15) |
| V, $Å^3$ | 3866 (3) | 3750.0 (4) |
| M–centroid, Å | 1.876[b] | 1.797[b] |

[a] Reference 28. [b] Reference 27.

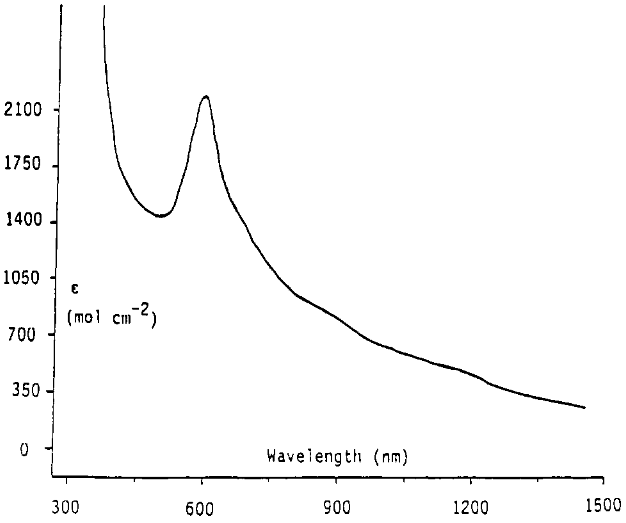

Figure 3. Electronic spectrum of [(η-$C_5(CH_3)_5$)Cr($\mu_3$-O)]$_4$ (3) in $CCl_4$ solution.

It is clear from the above that steric factors do not determine the geometry of the [Cr($\mu_3$-O)]$_4$ core of 1, 2, or 3. For this reason the disorder in ring 2 of 3 does not affect the metrical parameters of the core either. In 3 the Cr–Cr distances average 2.834 (2, 3, 6) Å, the Cr–O distances, 1.945 (5, 10, 25) Å, the Cr–O–Cr angles, 93.5 (2, 6, 12)°, and the O–Cr–O angles, 86.4 (2, 5, 9)°. It is seen that 3 has $T_d$ symmetry to a very close approximation, and only the 3.5° difference from 90° of the Cr–O–Cr and O–Cr–O angles prevents the [Cr($\mu_3$-O)]$_4$ core from being a perfect cube. Table I shows that the Cr–O, Cr–C, and Cr–C(ring) centroid distances in 1–3 are the same within experimental error. The differences in the symmetries ($D_2$ for 1, $D_{2d}$ for 2, and $T_d$ for 3) lies in the Cr–O–Cr and O–Cr–O angles. The O–Cr–O angles in 1 have average values of 83.24 (7) (×2), 86.30 (7) (×2), and 90.15 (7)° (×2); in 2 these angles are 83.9 (3) (×2) and 89.3 (3)° (×4), compared to 86.4 (2)° (×6) in 3. The Cr–O–Cr angles are 88.79 (7) (×2), 93.65 (7) (×2), and 96.64 (7)° (×2) in 1, 90.3 (3) (×4) and 95.8 (3)° (×2) in 2, and 93.5 (2)° (×6) in 3. The differences are very large (6–8°) compared to the errors (0.1–0.3°). As indicated below, there is evidence that 1 and 3 have the

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(26) Johnson, C. K. ORTEP-II: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(27) The three partially occupied $C_5Me_5$ rings in 4 have Cr–ring centroid distances of 1.757, 1.837, and 1.937 Å. The corresponding Cr–$C_5$ ring plane distances are 1.788, 1.845, and 1.812 Å. From the coordinates given in ref 28, V–ring centroid distances of 1.880, 1.951, and 1.872 Å may be calculated for (η-$C_5(CH_3)_5$)$_2$V; the corresponding V–$C_5$ ring plane distances are 1.842, 1.852, and 1.882 Å. In both the V and Cr cases there is a discrepancy between one of the three centroid and plane distances. The probable reason for this discrepancy is an inaccurately located C atom in a general position. This atom would have a greater affect on the centroid than on the plane distance. We believe that the best estimates are a Cr–ring centroid distance of 1.797 Å and a plane distance of 1.815 Å for 4 and corresponding distances of 1.876 and 1.859 Å for (η-($C_5$-$(CH_3)_5$)$_2$V.

(28) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739.

(29) Gard, E.; Haaland, A.; Novak, D. P.; Seip, R. *J. Organomet. Chem.* **1975**, *88*, 181.

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same structure in solution. This suggests that the differences in the angles are due to packing forces.

**Electronic Spectrum of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3).** The electronic spectrum of 3 in the visible and near-infrared regions (measured in $CCl_4$ solution) is shown in Figure 3. In essence, there is a single absorption band at 596 nm ($\epsilon = 2250$), with indications of several weaker bands at lower energy. The spectrum is very similar to that of 1, for which the main band was observed at 575 nm ($\epsilon = 3150$). The red shift of 21 nm on going from 1 to 3 is significant; the apparent difference in extinction coefficient is not significant, since no correction was made for the effect of the very intense absorptions due to the $\eta\text{-}C_5R_5$ ligands (R = H, Me).

There are three possible reasons for the red shift. The first is that there are different contributions of $\eta\text{-}C_5R_5$ orbitals to the $[Cr(\mu_3\text{-}O)]_4$ levels. Although the extended Hückel calculations, which have been used to describe the electronic structure of 1 and 3, are not appropriate for assigning the electronic spectrum, they do indicate that there is a negligible contribution of the $\eta\text{-}C_5R_5$ orbitals to the core levels. Also, it is generally accepted that $\eta\text{-}C_5(CH_3)_5$ produces a stronger ligand field than $\eta\text{-}C_5H_5$.[31] This would result in a blue shift on going from 1 to 3. We conclude, in agreement with the conclusions from the structural data, that the $\eta\text{-}C_5R_5$ ligand has a negligible effect on the $[Cr(\mu_3\text{-}O)]_4$ core. The second reason is that the red shift on going from 1 to 3 is caused by their different symmetries. However, the similarity of their electronic spectra indicates that 1 and 3 may, in fact, have the *same* symmetry in solution. It was noted previously that the NMR spectra indicated that the apparent symmetry of 1 in solution was $T_d$.[3] The third reason is that the red shift is caused, not by changes in the $[Cr(\mu_3\text{-}O)]_4$ core, but by changes in the high-energy, high-intensity, absorption bands that are due to transitions localized within the $\eta\text{-}C_5R_5$ ligands. That this is the correct reason is supported by the fact that the charge-transfer band in $(\eta\text{-}C_5H_n(CH_3)_{5-n})TiCl_3$ red shifts from 384 nm when $n = 5$ to 438 nm when $n = 0$.[32]

**Magnetic Properties of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3).** The ESR spectrum of 3 showed only a very broad featureless signal at both 295 and 80 K, indicative of a species with more than one unpaired electron and a short electronic relaxation time. The magnetic moment of 3 in solution (Evans NMR method[33]) at 295 K was 3.61 $\mu_B$. In the solid state (Faraday method) at 295 K the value was 3.74 $\mu_B$. The most detailed information was obtained from 4 to 85 K; the results are shown in Figure 4. It is seen that 3 is antiferromagnetic, the magnetic moment increasing from 1.10 $\mu_B$ at 4.5 K to 1.94 $\mu_B$ at 84.5 K. The magnetic moment was not field dependent. The antiferromagnetic behavior of 3 is the same as was observed for 1. There is, however, the difference that 3 is not diamagnetic even at 4.5 K, whereas 1 was diamagnetic below approximately 50 K.[3] In the higher temperature regions the magnetic moment of 3 was always higher than of 1 (e.g. 1.94 versus 1.10 at 84 K and 3.74 versus 3.15 at 295 K). We conclude that there is a higher population of the paramagnetic state at all temperatures in 3 compared to 1. This implies that the energy levels which can be thermally populated are closer together in 3 than in 1, due to the different symmetries in the solid state.

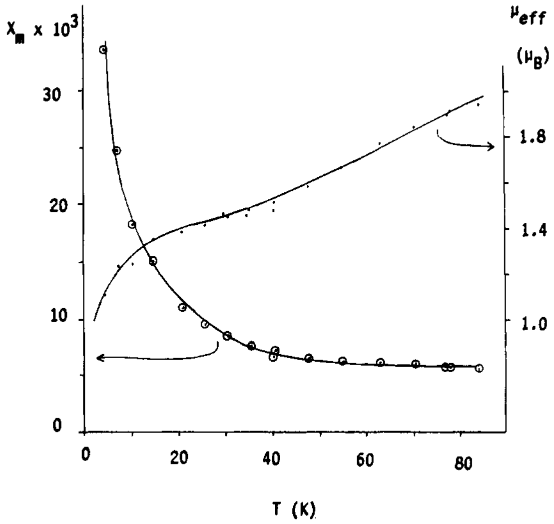

Figure 4. Magnetic behavior of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ over the temperature range 4–85 K.

## Experimental Section

**General Considerations.** All operations were conducted under argon or vacuum. Solvents were predried, stored over a drying agent, and distilled directly onto the reagents under vacuum. The starting material $(\eta\text{-}C_5(CH_3)_5)_2Cr$ (4) was prepared identically with the literature preparation of $(\eta\text{-}C_5(CH_3)_5)_2V$,[34] except that $LiC_5(CH_3)_5$ was used instead of the Na salt and $CrCl_3$ instead of $VCl_3$. Instruments used were a Perkin-Elmer 330 UV–visible–near-infrared spectrophotometer, a Perkin-Elmer 683 infrared spectrometer, a Varian XL-200 NMR spectrometer, a Varian E4 ESR spectrometer, and a Kratos MS50 mass spectrometer. Magnetic susceptibilities over the temperature range 4.4–85 K were made by using a Princeton Applied Research Model 155 vibrating sample magnetometer with an applied field of 9225 G. The equipment and calibration procedures were described previously.[35] Molar magnetic susceptibilities were corrected for the dimagnetism of the metal ($Cr^{3+}$) and ligands ($C_5(CH_3)_5^-$ and $O^{2-}$): $462 \times 10^{-6}$ cm$^3$ mol$^{-1}$.[36] Microanalyses were by Beller Labs, Göttingen, Germany.

**Reaction between $(\eta\text{-}C_5(CH_3)_5)_2Cr$ (4) and $N_2O$: Formation of $[(\eta\text{-}C_5(CH_3)_5)Cr(\mu_3\text{-}O)]_4$ (3).** A solution of 4 (4.50 g, 14.0 mmol) in toluene (100 mL) was incubated with $N_2O$ (21.0 mmol) at 80 °C for 8 days. Over this period the color of the solution gradually changed from red to dark green. On slow cooling, a green-black crystalline precipitate formed, which was removed by filtration. The precipitate was purified by first adding toluene (400 mL) in three portions, each portion being removed by evacuation.[37,38] The resultant solid was extracted twice with 150 mL portions of hexane, and then dissolved in either toluene (400 mL) or $CHCl_3$ (50 mL). The solution was filtered, the filtrate concentrated to half-volume, and hexane (200 mL in the case of the toluene solution, 100 mL in the case of $CHCl_3$) layered on the concentrated solution. After setting aside at room temperature for several days, crystalline 4 precipitated. This was collected by filtration. Yield: 1.10 g, 1.35 mmol, 39%. Anal. Calcd for $C_{40}H_{60}Cr_4O_4$: C, 59.1; H, 7.45. Found: C, 59.3; H, 7.4. Mass spectrum (FAB) [*m/e*, relative intensity (%) (assignment)]: 813, 100 ($[M + H]^+$); 677, 15 ($[M - C_5(CH_3)_5 + H]^+$); 660, 9 ($[M - C_5(CH_3)_5 - O]^+$); 525, 14 ($[M - 2(C_5(CH_3)_5) - O]^+$); 406, 8 ($[M - 3(C_5(CH_3)_5)]^+$); 390, 12 ([M –

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[37] This procedure removed the $(C_5(CH_3)_5)_2$ formed in the reaction; $(C_5(CH_3)_5)_2$ is a high-boiling oil, miscible with most organic solvents. It is therefore difficult to remove by conventional methods. A similar procedure for the removal of tetrahydrofuran has been described.[38]

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$3(C_5(CH_3)_5) - O]^+$); 273, 9 ($[Cr_4O_4 + H]^+$). Infrared spectrum (KBr disk): 550 cm$^{-1}$, s ([Cr($\mu_3$-O)]$_4$ antitranslation mode). Electronic spectrum: $\lambda_{max}$ 596 nm, $\epsilon = 2250$ in $CCl_4$ solution (see Figure 3). NMR spectrum ($^1$H, 200 MHz): −6.5 ppm, broad ($C_6D_6$ solution); −2.1 ppm, broad ($CDCl_3$ solution).

**Reaction between ($\eta$-$C_5(CH_3)_5)_2$Cr (4) and $O_2$: Formation of [($\eta$-$C_5(CH_3)_5$)Cr(O)($\mu$-O)]$_2$.** A solution of 4 (0.91 g, 2.83 mmol) in toluene (200 mL) was incubated with $O_2$ (11.3 mmol) for 12 h at room temperature. The resultant mixture was loaded onto a silica gel column and eluted with THF/hexane (1:10). The initial yellow band was discarded, the second blood-red band was collected and subjected to TLC, again using THF/hexane (1:5) as the eluent. The first band was again discarded, the second was extracted with THF. Slow evaporation gave orange-red crystals of [($\eta$-$C_5(CH_3)_5$)Cr(O)($\mu$-O)]$_2$ in 17% yield. The compound was identified by the following: microanalysis [Anal. Calcd for $C_{20}H_{30}Cr_2O_4$: C, 54.8; H, 6.9. Found: C, 55.1; H, 7.2]; NMR ($^1$H, 200 MHz, $CDCl_3$) 1.82 ppm; infrared 905 cm$^{-1}$ ($\nu$(Cr=O)). It was also identified by comparison of the crystal parameters with the literature. The crystals had the following cell dimensions: $a$ = 8.291 (2) Å, $b$ = 8.584 (2) Å, $c$ = 9.272 (5) Å, $\alpha$ = 98.39 (3)°, $\beta$ = 108.22 (3)°, $\gamma$ = 117.97 (1)°, space group $P\bar{1}$. The literature values are as follows: $a$ = 8.270 (2) Å, $b$ = 8.575 (2) Å, $c$ = 9.275 (4) Å, $\alpha$ = 98.78 (4)°, $\beta$ = 108.14 (2)°, $\gamma$ = 117.77 (3)°, space group $P\bar{1}$.[24]

**Oxidation of [($\eta$-$C_5H_5$)Cr($\mu_3$-O)]$_4$ (1) with $O_2$: Formation of $[Cr_2O_3(THF)_6]_n$.** To a solution of 1 (0.3 g, 0.56 mmol) in toluene (50 mL) was added $O_2$ (2.80 mmol). The blue solution turned brown immediately and began depositing a brown solid. The mixture was stirred for 4 h (room temperature) and then filtered, giving a brown residue. This solid was suspended in THF (100 mL) and the mixture refluxed for 5 days. Filtration gave $[Cr_2O_3(THF)_6]_n$ as a brown residue. Yield: 0.26 g, 39%. Anal. Calcd for $C_{24}H_{48}Cr_2O_9$: C, 48.0; H, 5.2; Cr (as $Cr_2O_3$), 18.0. Found: C, 49.3; H, 4.8; Cr, 17.8. Magnetic moment: 2.24 $\mu_B$ (295 K). Infrared: 550 cm$^{-1}$ ($\nu_{assym}$(Cr–O–Cr)). NMR ($^2H_6$ DMSO, 200 MHz): −32 ppm, very broad.

**Reaction of $[Cr_2O_3(THF)_6]_n$ with $SOCl_2$: Formation of $CrCl_3(THF)_3$.** To a suspension of $[Cr_2O_3(THF)_6]_n$ (0.96 g) in THF (100 mL) was added $SOCl_2$ (2.0 mL). The mixture was stirred for 12 h at room temperature and then filtered. The red-brown filtrate was evaporated to dryness in vacuo and the residue extracted with toluene (100 mL) to give a blue solution. After filtration the blue solution was concentrated to 20 mL in vacuo, layered with hexane (50 mL), and set aside. Purple crystals of $CrCl_3(THF)_3$ (0.25 g, 41%) deposited over 12 h. The product was identified by mass spectroscopy [$m/e$ 341 ($[CrCl_2(THF)_3 + H]^+$), 307 ($[CrCl(THF)_3]^+$)], microanalysis (Anal. Calcd for $C_{12}H_{24}Cl_3CrO_3$: C, 38.5; H, 6.5. Found: C, 38.0; H, 6.6), and comparison of the cell dimensions and space group of the crystals with the literature[25] ($a$ = 8.715 (1) Å, $b$ = 12.786 (3) Å, $c$ = 15.122 (3) Å, $\beta$ = 92.15 (1)°, space group $P2_1/c$. Found: $a$ = 8.7363 (7) Å, $b$ = 12.8049 (10) Å, $c$ = 15.1328 (10) Å, $\beta$ = 92.147 (6)°, space group $P2_1/c$).

**X-ray Diffraction Experiments.** The structures of 3 and 4 were determined at 295 K by using an Enraf-Nonius CAD4 diffractometer running under the control of the NRCCAD program.[39] The scan mode was $\theta/2\theta$, the radiation was Mo K$\alpha$ ($\lambda$ = 0.71073), and the structures were refined by using the NRCVAX program suite,[40] with scattering factors (corrected for anomalous dispersion except in the case of H) taken from ref 41.

**Crystal Data for 3:** $C_{40}H_{60}Cr_4O_4$, $M_r$ = 813.00; triclinic, $P\bar{1}$ (see the discussion of alternate space groups below); $a$ = 10.876 (2) Å, $b$ = 10.923 (2) Å, $c$ = 18.105 (2) Å, $\alpha$ = 83.75 (1)°, $\beta$ = 83.89 (1)°, $\gamma$ = 66.86 (1)°, $V$ = 1961.3 (5) Å$^3$; $Z$ = 2; $F_{000}$ = 856 electrons; $\mu$(Mo K$\alpha$) = 10.9 cm$^{-1}$; $D_{calcd}$ = 1.38 Mg m$^{-3}$. Cell dimensions were obtained from 20 reflections with $40 < 2\theta < 50°$. The crystal dimensions were 0.30 × 0.25 × 0.35 mm.

**Data Collection for 3.** A total of 8382 reflections were measured to $2\theta_{max}$ = 50° and averaged to yield 6890 unique reflections, of which 4121 were judged as observed by the criterion that $I > 2.5\sigma(I)$. The data were corrected for absorption by empirical methods (DIFABS[42]).

**Structure Determination of 3.** The cell dimensions given above can be translated to give a close approximation to a monoclinic cell ($a$ = 18.105 Å, $b$ = 12.010 Å, $c$ = 18.192 Å, $\beta$ = 97.41°). The dimensions are also very close to those of [$\eta$-$C_5(CH_3)_5$)V]$_4$($\mu_2$-O)$_6$ ($a$ = 11.077 (5) Å, $b$ = 11.113 (4) Å, $c$ = 18.394 (10) Å, $\alpha$ = 83.59 (4)°, $\beta$ = 83.73 (4)°, $\gamma$ = 66.62 (4)°[22]). In the latter case, a detailed investigation of the intensities of reflections which would be equivalent in a monoclinic space group was undertaken.[22] This showed that the triclinic description was correct beyond doubt. Since the dimensions of 3 are even further from monoclinic than was the case for [($\eta$-$C_5(CH_3)_5$)V]$_4$($\mu_2$-O)$_6$, the triclinic description was accepted for it also.

**Refinement of the Structure of 3.** All non-hydrogen atoms were refined anisotropically. Final refinement was by full-matrix methods with 463 parameters and a weighting scheme based on counting statistics ($w = 1/(\sigma(F)^2 + 0.001F^2)$). The final residuals were $R$ ($=\sum(|F_o| - |F_c|)/\sum|F_o|$) = 0.060, $R_w$ ($=[\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$) = 0.080, and GOF ($=[\sum w(|F_o| - |F_c|)^2/$(no. of reflections − no. of parameters)$]^{1/2}$) = 1.696. The largest $\Delta/\sigma$ was 0.31. A final difference Fourier synthesis had a maximum peak of 0.74 e Å$^{-3}$ and a deepest hole of −0.44 e Å$^{-3}$. The highest peak was located 0.74 Å from O(4) in the [Cr($\mu_3$-O)]$_4$ core. All of the 10 highest residual peaks were located within this core also.

During the refinement it became obvious that the $C_5(CH_3)_5$ ring attached to Cr(2) (ring 2) was severely disordered. The disorder was modeled with two sites for this ring (rotated 36° with respect to one another), with fixed site occupancies of 60:40%. The model was refined (after several trials) with the carbon atoms of ring 2 fixed in the positions they achieved in a refinement using isotropic temperature factors for carbon atoms C(21) through C(251A) (Table V). All carbon atoms were then refined anisotropically; the resultant $U_{ij}$ values are high for some of the carbon atoms of ring 2, indicating that the model was inadequate. More complicated models were unjustified by the data available. Considering the other $\eta$-$C_5(CH_3)_5$ rings, that attached to Cr(3) was very well behaved, that of Cr(4) was normal, and that of Cr(1) had large thermal parameters. All the $CH_3$ hydrogen atoms were readily located for rings 3 and 4, some were located for ring 1 and only a few for the disordered ring 2. The observed hydrogen atom positions were used to calculate the remaining positions where necessary. In the final refinement all hydrogen atoms were included as fixed contributions (C–H 0.96 Å, tetrahedral geometry, and a isotropic thermal parameters equal to that of the carbon atom to which they were attached). The positional parameters for the non-hydrogen atoms of 3 are given in Table V, and important distances and angles, in Table II. Complete details are available in the supplementary material.

**Crystal Data for 4:** $C_{20}H_{30}Cr$, $M_r$ = 322.45; orthorhombic, $Ccmm$ (see the discussion of alternate space groups below); $a$ = 8.6857 (5) Å, $b$ = 14.7842 (8) Å, $c$ = 29.2031 (15) Å, $V$ = 3750.0 (4) Å$^3$; Z = 8 (two independent molecules of ($\eta$-$C_5(CH_3)_5)_2$Cr per asymmetric unit, with four asymmetric units per unit cell); $F_{000}$ = 1392 electrons; $\mu$(Mo K$\alpha$) = 5.9 cm$^{-1}$; $D_{calcd}$ = 1.14 Mg m$^{-3}$. Cell dimensions were obtained from 25 reflections with $40 < 2\theta < 48°$. Crystal dimensions were 0.55 × 0.35 × 0.15 mm.

**Data Collection for 4.** A total of 1675 reflections were measured to $2\theta$ = 50° and averaged to yield 1664 unique reflections, of which 816 were judged observed ($I > 2.5\sigma(I)$). No absorption correction was made.

**Structure Determination of 4.** The cell dimensions, space group, and intensity profile for 4 are similar to those of ($\eta$-$C_5(CH_3)_5)_2$V.[28] As was the case for the vanadium complex, there are two independent molecules of 4 in the unit cell. Their locations are the same in both cases (note the nonstandard space group setting used in the present work). However, whereas in the vanadium complex the molecule lying on the $m2m$ position (position $c$ is the ref 41 description of $Ccmm$) was not disordered, in 4 both molecules were disordered and the disorder was com-

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**Table V. Positional Parameters and $B_{iso}$ Values[a] for the Non-Hydrogen Atoms of 3**

| | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| Cr(1) | 0.19491 (12) | 0.33416 (11) | 0.31920 (7) | 2.53 (6) |
| Cr(2) | 0.22430 (13) | 0.30314 (12) | 0.16447 (7) | 2.77 (6) |
| Cr(3) | 0.45201 (12) | 0.19713 (12) | 0.24985 (7) | 2.61 (6) |
| Cr(4) | 0.26040 (12) | 0.07833 (11) | 0.26725 (7) | 2.52 (6) |
| O(1) | 0.3633 (5) | 0.1307 (5) | 0.1854 (3) | 2.6 (3) |
| O(2) | 0.3033 (5) | 0.3708 (4) | 0.2340 (3) | 2.47 (24) |
| O(3) | 0.3351 (5) | 0.1600 (4) | 0.3306 (3) | 2.55 (24) |
| O(4) | 0.1220 (5) | 0.2590 (5) | 0.2507 (3) | 2.64 (24) |
| C(11) | 0.1822 (10) | 0.3892 (8) | 0.4378 (5) | 3.9 (5) |
| C(111) | 0.2827 (13) | 0.3072 (11) | 0.4931 (6) | 7.4 (7) |
| C(12) | 0.1826 (9) | 0.4971 (8) | 0.3897 (5) | 3.8 (4) |
| C(121) | 0.2825 (11) | 0.5651 (11) | 0.3832 (7) | 6.4 (7) |
| C(13) | 0.0706 (9) | 0.5434 (8) | 0.3505 (5) | 4.0 (5) |
| C(131) | 0.0278 (14) | 0.6711 (10) | 0.2978 (6) | 7.6 (8) |
| C(14) | −0.0050 (10) | 0.4633 (10) | 0.3732 (6) | 4.7 (5) |
| C(141) | −0.1375 (11) | 0.4776 (13) | 0.3465 (7) | 8.1 (8) |
| C(15) | 0.0670 (9) | 0.3660 (9) | 0.4274 (5) | 4.1 (5) |
| C(151) | 0.0204 (16) | 0.2683 (12) | 0.4742 (7) | 9.7 (10) |
| C(21) | 0.1772 | 0.4883 | 0.0825 | 3.3 (10) |
| C(211) | 0.2169 | 0.6045 | 0.0950 | 9.1 (17) |
| C(22) | 0.2687 | 0.3748 | 0.0451 | 4.4 (12) |
| C(221) | 0.4080 | 0.3583 | 0.0092 | 10.5 (19) |
| C(23) | 0.2049 | 0.2866 | 0.0430 | 3.2 (10) |
| C(231) | 0.2607 | 0.1541 | 0.0101 | 9.6 (15) |
| C(24) | 0.0745 | 0.3423 | 0.0784 | 3.3 (10) |
| C(241) | −0.0485 | 0.3046 | 0.0900 | 7.1 (13) |
| C(25) | 0.0523 | 0.4688 | 0.1019 | 3.4 (9) |
| C(251) | −0.0698 | 0.5645 | 0.1343 | 7.7 (11) |
| C(21A) | 0.2337 | 0.4359 | 0.0620 | 4.9 (22) |
| C(211A) | 0.3552 | 0.4775 | 0.0489 | 10.2 (30) |
| C(22A) | 0.2663 | 0.3016 | 0.0383 | 4.1 (16) |
| C(221A) | 0.3910 | 0.2060 | −0.0039 | 10.7 (25) |
| C(23A) | 0.1493 | 0.2773 | 0.0579 | 3.1 (14) |
| C(231A) | 0.1022 | 0.1638 | 0.0416 | 13.0 (40) |
| C(24A) | 0.0475 | 0.3980 | 0.0903 | 4.9 (18) |
| C(241A) | −0.0910 | 0.4277 | 0.1195 | 13.6 (41) |
| C(25A) | 0.1113 | 0.4785 | 0.0943 | 3.9 (17) |
| C(251A) | 0.0714 | 0.6246 | 0.1108 | 15.1 (43) |
| C(31) | 0.6518 (7) | 0.1676 (9) | 0.1838 (5) | 3.5 (4) |
| C(311) | 0.6746 (10) | 0.1707 (12) | 0.1005 (6) | 6.6 (7) |
| C(32) | 0.6669 (8) | 0.0520 (9) | 0.2296 (5) | 3.6 (4) |
| C(321) | 0.7037 (10) | −0.0830 (10) | 0.2000 (6) | 5.9 (6) |
| C(33) | 0.6460 (7) | 0.0841 (8) | 0.3041 (5) | 3.5 (4) |
| C(331) | 0.6565 (10) | −0.0095 (10) | 0.3735 (5) | 5.3 (5) |
| C(34) | 0.6206 (8) | 0.2195 (9) | 0.3049 (5) | 3.8 (4) |
| C(341) | 0.6041 (10) | 0.2925 (12) | 0.3746 (6) | 6.3 (6) |
| C(35) | 0.6213 (8) | 0.2748 (9) | 0.2314 (6) | 4.1 (5) |
| C(351) | 0.5960 (10) | 0.4162 (11) | 0.2061 (7) | 6.4 (7) |
| C(41) | 0.2424 (10) | −0.0848 (8) | 0.3523 (5) | 3.8 (5) |
| C(411) | 0.2564 (15) | −0.0841 (11) | 0.4335 (6) | 8.0 (9) |
| C(42) | 0.1257 (9) | −0.0282 (8) | 0.3159 (6) | 4.4 (5) |
| C(421) | −0.0132 (12) | 0.0402 (12) | 0.3499 (9) | 8.9 (9) |
| C(43) | 0.1579 (11) | −0.0562 (9) | 0.2401 (6) | 4.7 (5) |
| C(431) | 0.0524 (14) | −0.0203 (13) | 0.1830 (8) | 9.3 (10) |
| C(44) | 0.2958 (10) | −0.1280 (8) | 0.2312 (5) | 4.0 (5) |
| C(441) | 0.3764 (14) | −0.1800 (11) | 0.1601 (6) | 7.6 (8) |
| C(45) | 0.3477 (9) | −0.1442 (8) | 0.2993 (6) | 4.2 (5) |
| C(451) | 0.4911 (11) | −0.2282 (10) | 0.3184 (8) | 7.4 (8) |

[a] $B_{iso}$ (Å$^2$) is the mean of the principal axes of the thermal ellipsoid.

**Table VI. Positional Parameters and $B_{iso}$ Values[a] for the Non-Hydrogen Atoms of 4**

| | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| Cr(1) | 0.8278 (3) | 0 | 0.25 | 4.04 (15) |
| C(11) | 0.9615 (24) | 0.1228 (14) | 0.25 | 5.0 (5) |
| C(12) | 0.8633 (19) | 0.1196 (8) | 0.2121 (4) | 3.8 (3) |
| C(13) | 0.7046 (19) | 0.1159 (10) | 0.2258 (6) | 5.2 (3) |
| C(14) | 0.955 (6) | 0.116 (3) | 0.2257 (15) | 4.9 (9) |
| C(15) | 0.778 (6) | 0.128 (3) | 0.2134 (14) | 4.2 (9) |
| C(16) | 0.708 (7) | 0.133 (4) | 0.25 | 5.5 (15) |
| C(111) | 1.121 (3) | 0.1288 (16) | 0.25 | 9.2 (6) |
| C(121) | 0.927 (3) | 0.1222 (14) | 0.1626 (8) | 10.7 (6) |
| C(131) | 0.5650 (19) | 0.1207 (11) | 0.1986 (6) | 8.8 (4) |
| C(141) | 1.119 (7) | 0.129 (4) | 0.1988 (22) | 8.9 (16) |
| C(151) | 0.840 (5) | 0.138 (3) | 0.1638 915) | 11.3 (12) |
| Cr(2) | 0.5 | 0 | 0 | 4.11 (13) |
| C(21) | 0.6750 (20) | 0.0474 (10) | 0.0464 (5) | 3.32 (23) |
| C(22) | 0.5139 (24) | 0.0743 (15) | 0.0623 (7) | 6.4 (5) |
| C(23) | 0.4385 (15) | 0.0339 (7) | 0.0709 (4) | 3.3 (3) |
| C(24) | 0.5797 (22) | 0.0806 (11) | 0.0571 (6) | 2.2 (3) |
| C(25) | 0.682 (5) | 0 | 0.0504 (14) | 7.6 (11) |
| C(211) | 0.834 (3) | 0.0941 (17) | 0.0325 (8) | 8.5 (6) |
| C(221) | 0.540 (3) | 0.1863 (14) | 0.0623 (7) | 7.8 (5) |
| C(231) | 0.293 (3) | 0.0799 (20) | 0.0861 (10) | 12.2 (8) |
| C(241) | 0.668 (7) | 0.168 (3) | 0.0541 (17) | 5.6 (11) |
| C(251) | 0.847 (8) | 0 | 0.0388 (21) | 7.0 (15) |
| C(261) | 0.754 (6) | 0.138 (3) | 0.0377 (16) | 4.9 (10) |
| C(271) | 0.413 (6) | 0.162 (3) | 0.0729 (16) | 5.7 (11) |
| C(281) | 0.286 (5) | 0 | 0.0899 (16) | 4.6 (11) |

[a] $B_{iso}$ (Å$^2$) is the mean of the principal axes of the thermal ellipsoid.

plicated. The $C_5$ rings could be modeled by two sites with a rotation of 36°, but the $CH_3$ groups could not be so simply accommodated. In one molecule only nine partially occupied $CH_3$ positions were evident, in the other a total of 14. Occupancies were estimated from the relative peak heights in a difference Fourier synthesis but were not refined. Several trial refinements were attempted before the one used was adopted. Refinement using anisotropic temperature factors for the carbon atoms led to impossible thermal ellipsoids. Refinement in the other possible space groups (*Ccm*2$_1$ and *Cc*2*m*) was tried, but the disorder persisted, and the additional parameters required by these space groups could not be justified by the data available.

**Refinement of the Structure of 4.** The Cr atoms were refined anisotropically; all other non-hydrogen atoms, isotropically. Final refinement (full matrix) used 100 parameters and a weighting scheme as for 3 and gave $R = 0.079$, $R_w = 0.092$, and GOF = 1.946. The largest $\Delta/\sigma$ was 0.63. The maximum peak in the difference Fourier synthesis was 0.37, and the deepest hole was −0.38 e Å$^{-3}$. The peak was located near a $CH_3$ group. Hydrogen atoms, included as fixed contributions, significantly improved the agreement and were therefore included, with the geometry as described for 3, in the final refinement. Positional parameters for the non-hydrogen atoms of 4 are given in Table VI.

## Conclusions

The nature of the $\eta$-$C_5R_5$ ligand does not affect the structure of the $[Cr(\mu_3\text{-}O)]_4$ core of $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$. The different symmetries (R = H, $D_2$; $R_5 = H_4CH_3$, $D_{2d}$; R = $CH_3$, $T_d$) are not due to steric factors. It is possible that all three cubanes have the same symmetry in solution. The different symmetries observed in the solid state must be due to differences in crystal packing. The $\eta$-$C_5(CH_3)_5$ ligand in 3 is not removed from the core by oxidation, in contrast to $\eta$-$C_5H_5$ in 1.

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**Note Added in Proof:** We have now prepared 3 from the reaction of $[(\eta\text{-}C_5(CH_3)_5)CrCl(\mu\text{-}Cl)]_2$ and $Ag_2(CO_3)$ in tetrahydrofuran.

**Supplementary Material Available:** Diagrams of the numbering schemes and lists of hydrogen atom positions, $U_{ij}$ values, bond distances and angles, and distances to the least-squares planes for 3 and 4 (17 pages); lists of observed and calculated structure factors for 3 and 4 (24 pages). Ordering information is given on any current masthead page.