Preparation and Structure of $(\eta^5\text{-}C_5H_5)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$, a Hydrocarbon Derivative of the Cubane Cluster $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$

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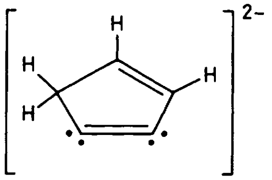
Oxidation of $(cp)_2Cr$ (cp = $\eta^5\text{-}C_5H_5$) with Me_3NO produces a mixture of the previously reported $(cp)_4Cr_4O_4$ and $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$; the structure of the latter has been determined by *X*-ray crystallography.

In previous papers we described the preparation and structure of the cubane cluster $(cp)_4Cr_4O_4$ (cp = $\eta^5\text{-}C_5H_5$), obtained from the reaction between N_2O and $(cp)_2Cr$.[1,2] This reaction also produced a small quantity of a green material which we were unable to separate from $(cp)_4Cr_4O_4$, but which we surmised to be another $(cp)_mCr_mO_n$ cluster because of the similarity of its physical and chemical properties to those of $(cp)_4Cr_4O_4$.[2] We show here that this green compound is $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$, a derivative of $(cp)_4Cr_4O_4$, containing the η^2-ligand (**1**). This compound provides the first example of an oxide cluster in which one oxygen atom has been replaced by an electronically equivalent organic ligand; the replacement of oxygen by an organic ligand in a monomeric complex has been reported recently.[3]

When $(cp)_2Cr$ is oxidised with Me_3NO a mixture of $(cp)_4Cr_4O_4$ and a dark green compound is obtained. This result is the same as when N_2O was used as oxidant, but with Me_3NO the proportion of the green compound in the product is much higher. Because $(cp)_4Cr_4O_4$ is marginally less soluble, a toluene solution of a mixture of the compounds deposits blue crystals of $(cp)_4Cr_4O_4$ on the bottom of the flask but green crystals on the upper walls close to the surface of the liquid. We have also achieved a separation using chromatography on glass beads with diethyl ether and tetrahydrofuran as eluants.



(**1**)

The structure determination by *X*-ray diffraction shows that the green compound is the cluster $[(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)]$ (Figure 1), which is derived from $(cp)_4Cr_4O_4$ by formal

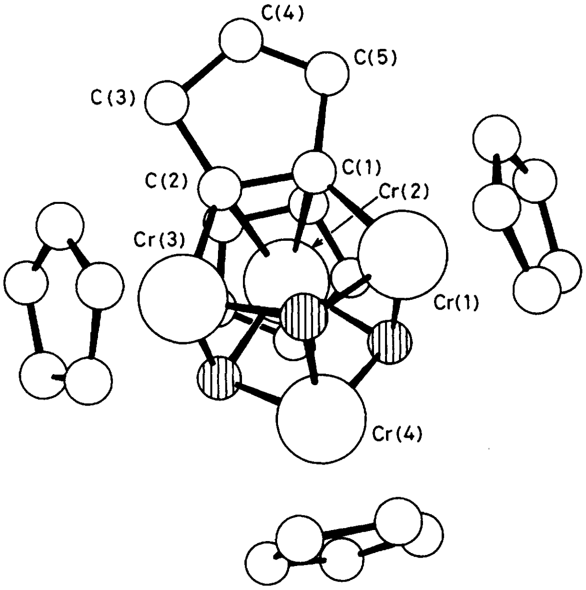


Figure 1. The molecular structure of $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ and the atom numbering scheme. Important dimensions (average of the two independent molecules) are: Cr(1)–C(1) 1.97(5); Cr(2)–C(1) 2.15(5); Cr(2)–C(2) 2.22(5); Cr(3)–C(2) 2.04(4); C(1)–C(2) 1.36(8); C(2)–C(3) 1.57(7); C(3)–C(4) 1.47(7); C(4)–C(5) 1.43(8); C(5)–C(1) 1.61(5) Å; C(1)–C(2)–C(3) 113(4); C(2)–C(3)–C(4) 101(4); C(3)–C(4)–C(5) 115(4); C(4)–C(5)–C(1) 103(4); C(5)–C(1)–C(2) 107(4)°.

replacement of one O^{2-} by the dinegative ligand (**1**); (**1**) is bonded in the dihapto mode to three Cr atoms. Valence bond representations of the cluster core are shown in Figure 2. The formal count of 60 electrons for the cluster and 12 for the metal cluster orbitals[4] is the same in $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ as in $(cp)_4Cr_4O_4$. In contrast to $(cp)_4Cr_4O_4$ which has a distorted tetrahedral arrangement of the Cr atoms in the Cr_4O_4 cube (D_2 symmetry, Cr–Cr distances ranging from 2.70 to 2.90 Å), $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ has a definite butterfly geometry. The Cr(1)–Cr(3) distance, which is spanned by the hydrocarbon bridge, is 3.28 Å; the Cr(2)–Cr(4) distance is 2.87 Å; the other four Cr–Cr distances are in the range 2.70—2.77 Å.

Crystal data: $C_{25}H_{24}Cr_4O_3$, monoclinic, $P2_1/c$, $a = 18.724(8)$, $b = 13.592(7)$, $c = 19.562(10)$ Å, $\beta = 115.63(4)°$, $Z = 8$. The crystals were very small and gave only limited diffraction data [2103 of the 5864 independent reflections with $2\theta \leqslant 45°$ were 'observed' with $I > \sigma(I)$]. In addition there are two independent molecules of $(C_5H_5)_4Cr_4O_3(C_5H_4)$ in the asymmetric unit. Least squares refinement of the data collected on a Picker FACS 1 diffractometer converged at $R = 0.127$.†

Green $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ has magnetic properties. Both n.m.r. and e.s.r. spectra show very broad featureless signals which cannot be analysed in detail. Like $(cp)_4Cr_4O_4$ the new cluster appears to be antiferromagnetic with a very high Néel temperature. The i.r. spectrum in the C–H stretching region shows a weak band at 3025 cm^{-1} and at least four intense broad bands between 2850 and 2960 cm^{-1}, due to the $\eta^2\text{-}C_5H_4$ ligand. In contrast $(cp)_4Cr_4O_4$ shows only two weak sharp bands at 3050/3040 cm^{-1} and 2955 cm^{-1}. The mass spectrum shows a molecular ion peak at *m/z* 580; fragments involving loss of cp from the cluster and/or H from the $\eta^2\text{-}C_5H_4$ ligand are observed also. The bonding between the chromium atoms and the C_5H_4 ligand is evidently strong, since both $Cr_3(C_5H_4)$ and $Cr_3(C_5H_3)$ fragments are observed. As with $(cp)_4Cr_4O_4$, the thermal stability is remarkable; no mass spectrum is observed below 150 °C and sublimation at 10^{-1} Torr occurs only above 300 °C. However the $\eta^2\text{-}C_5H_4$ ligand (**1**) is readily lost on oxidation. Reagents containing oxygen convert $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ into $(cp)_4Cr_4O_4$, and in that sense the former is an intermediate in the formation of the latter.

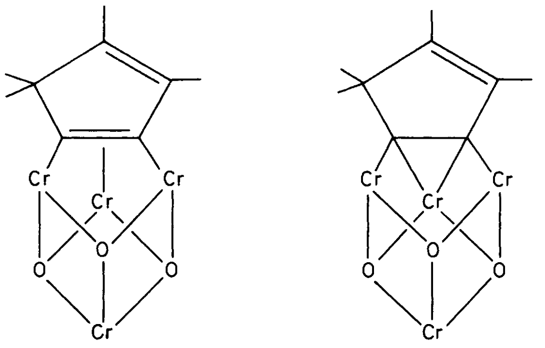


Figure 2. Valence bond representations of the bonding in the $Cr_4O_3(\eta^2\text{-}C_5H_4)$ core of $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$.

This $(cp)_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ cluster can be regarded as a model for alkene binding to a metal oxide, and we are continuing to investigate its magnetic properties and the reactivity of the $\eta^2\text{-}C_5H_4$ ligand.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory. Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.