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THE CRYSTAL STRUCTURE OF TETRAKIS(2-METHYL-2-PHENYLPROPYL)CHROMIUM

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SUMMARY

X-ray structure determination of $Cr(CH_2CMe_2Ph)_4$ shows the Cr^{IV} to be coordinated by a slightly distorted tetrahedron of carbon atoms. The mean Cr–C distance was found to be 2.05 Å.

Tetrakis(2-methyl-2-phenylpropyl)chromium which was first isolated by Mowat and Wilkinson[1] shows a remarkable chemical inertness. In benzene solution it is decomposed by concentrated sulphuric acid at room temperature only after several hours. We have investigated the crystal structure in order to check if the steric arrangement of the alkyl and aryl groups is responsible for this low reactivity.

For the present investigation, flat purple prisms obtained from a synthesis in our laboratory[2] were grown from pentane solution at about −40°. The crystals are monoclinic ($P\,2_1/c$) with 4 formula units per cell, $a=17.75$ Å, $b=9.86$ Å, $c=21.18$ Å, $\beta=129.9°$, (standard deviations less than 2%). Using a Picker four-circle diffractometer, 1837 reflections with $\theta \leqslant 16°$(Mo-K_α) were measured from a crystal sealed in a glass tube under nitrogen. 400 reflections were observed to be less than their estimated standard deviation. The heavy atom method to solve the crystal structure did not result in an unambiguous first coordination sphere of the Cr atom nor in other chemically reasonable fractional parts of the molecule and was abandoned. Direct methods using the programs of the "XRAY" system[3] have then been successfully applied to solve the structure. Preliminary least-squares refinement led to a weighted $R=0.127$ for the observed reflections.

The Cr–C distances in the molecule shown in the figure were found to be 2.07, 2.06, 2.05 and 2.01 Å with mean standard deviations of 0.026 Å. The C–Cr–C angles were calculated as 114, 112, 111, 107, 106 and 105° with standard deviations of 1°. The Cr–C distances are therefore not significantly different but the bond angles are so. This is in agreement with the results of Ward *et al.*[4] who required some distortion of the *T* symmetry of the Cr atom to explain the observed EPR line broadening.

The deviation of all C–C bond lengths and C–C–C angles from those found in similar compounds is less than 3σ [average values σ(C–C) 0.04 Å, σ(C–C–C) 2°]. The planarity of the phenyl groups has been checked by least squares plane calculations with the result of a mean deviation of less than 0.02 Å (maximum 0.036 Å). The phenyl rings are all in nearly eclipsed conformation with respect to one of the corresponding methyl groups (mean deviation 8°).

The Cr–C–C angles are 126, 125, 124 and 119°, all values being significantly larger than the tetrahedral angle. This contrasts with the finding in several tetrabenzyls of Group IV metals[5,6] where some of the metal –C–C angles are less than 90°. All phenyl rings are turned toward the CH_2 groups bonded at the Cr atom (*cf.* Fig. 1) so that contact between the phenyl π-electrons and the hydrogen atoms of the CH_2 groups can be envisaged, as revealed by trial calculations of possible positions of these hydrogens. It should be mentioned however, that no possible contact between hydrogen atoms of the CH_2 groups and a phenyl ring has been found at the ligand C4.

The avoidance of too short distances may be one reason for the large values of the Cr–C–C angles. The relatively dense packing of alkyl and aryl groups can therefore be assumed to be at least partly responsible for the stability of the $Cr(CH_2CMe_2Ph)_4$ compound.

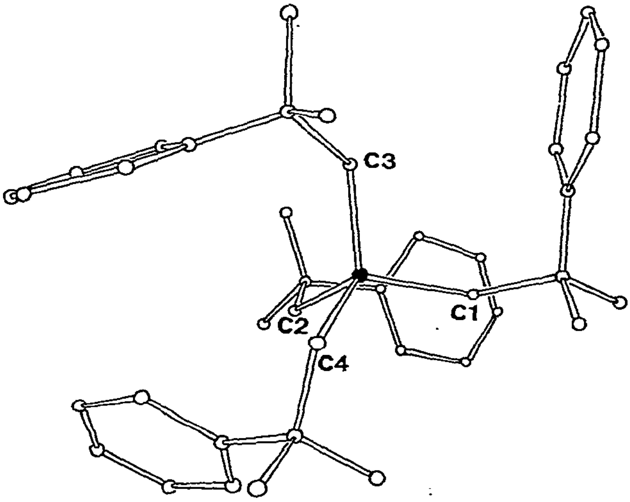

Fig. 1. $Cr(CH_2CMe_2Ph)_4$. The chromium atom is represented by the black dot.

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