Short Communication

The Molecular Structure of Tetrakis(neopentyl)chromium, Cr(CH₂CeMe₃)₄, Determined by Gas-Phase Electron Diffraction. Ab Initio Molecular Orbital Calculations on CrMe₄ and CrF₄

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By introducing a bulky neopentyl ligand, homoleptic monomeric alkyls have been isolated for several transition elements. The gas-phase molecular structure of monomeric Mn(CH₂CeMe₃)₄ has been published. The gas-phase structures of Cr(OBu)₄ and CrF₄, pseudo-isoelectronic with Cr(CH₂CeMe₃)₄, are also known. Tetrakis(neopentyl)chromium is sufficiently thermally stable for a gas-phase electron diffraction (GED) investigation. Although oxidation state IV is quite rare for chromium, this compound, along with other alkyls, amides and alkoxides of chromium(IV), is quite stable towards attack by water, alcohols, amines and phosphines.

Electron spin resonance spectra, electronic absorption spectra and the photoelectron spectra of Cr(CH₂CeMe₃)₄ are all consistent with a molecular model with a tetrahedral CrCe core and an electronic ^1A₁g(^2) ground state.

Information concerning the synthesis of the compound, the GED experiments, the data reduction and the ab initio calculations is given in the Appendix.

Model choice and refinements

Refinements were carried out on models with S₄, D₃d, C₃, and C₃ symmetry. Of these only the S₄ model, shown in Fig. 1, could be brought into satisfactory agreement with the experimental data, giving a final value of R of 0.045. Even though they require the refinement of a greater number of independent parameters, the other models yielded R factors ranging from 0.056 to 0.068.

The S₄ model was characterized by three independent bond distances, r(Cr–C), r(C–C) and r(C–H), and by four valence angles, ζ(C′–Cr–C), ζ(C–C–C′), ζ(C–C′–C) and ζ(C–C–H). The methylene protons were arbitrarily fixed in a plane bisecting ζ(Cr–C–C′) with ζ(C–C–H) = 109.47°. Initial refinements were carried out with ζ(C–C–C′) fixed at 109.47°. Subsequent refinements of this parameter did not improve the fit: it converged to ca. 110.7(2.2)° independently of the starting value. All refinements with this angle fixed at values smaller or greater than tetrahedral gave an increased R factor. In the final refinements ζ(C′–C–C) was again fixed at 109.47°. Refinements were also carried out on models in which the C–Me₃ fragments were allowed to tilt in the direction of increasing C–C and C–C distances. (In the final refinements the tilt angle θ was fixed at 1.5°.) The remaining two independent parameters are torsional angles: ϕ(C′–Cr–C–C′) and ϕ(Cr–C–C–C′).

Results and discussion

An experimental radial distribution curve and the corresponding curve calculated for the best model are compared in Fig. 2. Selected structure parameters and vibrational amplitudes are listed in Table 1. Least-squares standard

Fig. 1. Molecular model of Cr(CH₂CeMe₃)₄. Symmetry S₄.
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errors have been multiplied by a factor of three to compensate for data correlation and the assumptions made when defining the model. Of the correlation coefficients, only $r(\text{Cr}-\text{C})/r(\text{C}^*=\text{H})$ of 77% and $\angle \text{Cr}-\text{C}^*-\text{C}$ of −71% are of concern.

The Cr–C bond distance in Cr(CH$_2$CMe$_3$)$_2$ is in reasonable agreement with the bond distances found by X-ray crystallography in two other Cr(IV) tetraalkyls, the mean $r(\text{Cr}-\text{C})$ in Cr(CH$_2$CMe$_3$Ph)$_2$ is 205(3) pm, and the two crystallographically independent Cr–C bond distances in Cr(cyclo-C$_6$H$_{11}$)$_2$ are 201.0(4) and 200.9(4) pm, respectively. Other alkyls with chromium in lower oxidation states appear to have somewhat longer Cr–C bonds: the calculated (MCPF) Cr–C distance in CrMe$_2$, is 207 pm, and in Cr(II)(CH$_2$CMe$_3$)$_2$ dippe (a tetrahedrally distorted square-planar complex) Cr–C = 214.9(8) pm. The $\angle \text{Cr}$–C angle is significantly larger than the corresponding angle in Mn(CH$_2$CMe$_3$)$_2$, 120(7)$^\circ$,1 probably owing to additional steric strain introduced by both a shorter M–C bond and a larger number of bulky ligands.

We find no evidence for distortion from a tetrahedral Cr$_2$ core. Similar negative conclusions have been reached in spectroscopic studies.5,5 The crystal structures of Cr(CH$_2$CMe$_3$Ph)$_2$ and Cr(cyclo-C$_6$H$_{11}$)$_2$ indicate slightly flattened tetrahedral coordination geometries: the mean angles $\angle \text{C}$–Cr–C are 113° (Ref. 6) and 114° (Ref. 7), respectively. If these compounds have electronic ground states of $^3\Delta_1$ symmetry, the reason for the distortion must be sought in steric interaction between the ligands or between molecules.

Gas electron diffraction studies of Cr(OCMe)$_3$,2 and CrF$_2$, similarly failed to give evidence for distortion from tetrahedral coordination geometry. The bond distances to Cr are, however, much shorter than in the alkyls; Cr–O = 175.1(7) pm and Cr–F = 170.6(2) pm. The shortening may be due to the smaller covalent radii of O and F, to electro-negativity difference effects, and possibly to dative Cr–O and Cr–F $\pi$-bonding.

In order to elucidate possible $\pi$-bonding effects we carried out ab initio MO calculations on CrMe$_4$ and CrF$_4$. Total energies, optimized geometries, orbital energies and Mulliken parameters are listed in Table 2. The optimized bond distances are in good agreement with experimental values. The e(3d) and Cr–C ionization potentials determined from the photoelectron spectrum of Cr(CH$_2$CMe$_3$)$_2$ are 7.25 and 8.69 eV, respectively,3 much smaller than estimated from the orbital energies and Koopmans' theorem; relaxation energies are apparently not negligible. The effective atomic charges on Cr are +1.679 in CrMe$_4$ and +1.835 in CrF$_4$.

$\pi$-Interactions in tetrahedral systems are complicated to analyse. The ligand $\pi$-orbitals (transforming as $t_1+t_2+e$) may interact with both the $d(e^+t_2)$ and $p_e$ orbitals on the metal. The population of each of the $d(e)$ orbitals, usually considered as the $d_x$ orbitals, is indeed somewhat higher in CrF$_4$ than in CrMe$_4$, but the population of the $\sigma$-antibonding $d(t)$ is higher in CrMe$_4$ than in CrF$_4$. Our conclusion must again be put in the negative: the calculations do not provide clear-cut evidence for significant $\pi$-bonding in CrF$_4$.

### Appendix: Experiment, data processing and calculations

Cr(CH$_2$CMe$_3$)$_2$ was prepared from Me$_2$CCH$_2$Li and CrCl$_2$(thf)$_2$, as previously described.5 The compound was purified by crystallization from pentane as purple-red...
Table 2. Ab initio restricted Hartree–Fock calculations on Cr (CH₃)₆ and CrF₆, state A₄. Optimized geometry, Mulliken population parameters, orbital energies and total energies.

<table>
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<tr>
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<th>Cr(CH₃)₆</th>
<th>CrF₆</th>
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<tbody>
<tr>
<td>rₑₑₑ/Å</td>
<td>200</td>
<td>171</td>
</tr>
<tr>
<td>rₑₑₑ/Å</td>
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<td>C</td>
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<tr>
<td>F</td>
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<tr>
<td>H</td>
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<td>Orbital populations:</td>
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<tr>
<td>d(t₂)</td>
<td>0.613</td>
<td>0.415</td>
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<td>d(e)</td>
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<tr>
<td>a₁ (Cr-ligand bond)</td>
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<td>Total energy/a.u.</td>
<td>−1201.5462</td>
<td>−1441.1916</td>
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*From GED data on Cr(CH₃)₆, present work.

The GED data were recorded on a Balzers Eldigraph KDG-2. The nozzle and reservoir temperatures were about 130°C. The electronic wavelength has been calibrated against the C–C bond distance in gaseous benzene (rₑ = 139.75 pm). Two sets of data were recorded, four plates with a nozzle-to-plate distance of 50 cm, and four plates with a distance of 25 cm. The s-limits used in the final refinements were s = 30.0–140.0 nm⁻¹ with Δs = 1.25 nm⁻¹ (50 cm) and s = 30.0–220.0 nm⁻¹ with Δs = 2.50 nm⁻¹ (25 cm). After photometry on a Joyce–Loebel densitometer the data were processed by standard procedures. The backgrounds were drawn by computer, and finally the intensity curves were averaged within each set of data. Complex atomic scattering factors f(s) were taken from Ref. 13. The intensity curves for the best model are shown in Fig. 3.

Ab initio open-shell restricted Hartree–Fock calculations have been carried out on CrF₆ and CrMe₆ using the program DISCO. For both molecules we have chosen the state A₄ in the point group T₄. The Gaussian-type basis on chromium was [15, 9, 7], contracted to <12, 9, 5> taken from Ref. 15; a diffuse p-function with exponent 0.17 was added. The basis sets on carbon and fluorine were [9, 5], contracted to <4, 3> from Ref. 16, and on hydrogen [3], contracted to <2> from Ref. 17. The geometry was fixed with ωCr–C–H at 109.5° and the C–H bond distance at 109 pm. The Cr–C and Cr–F optimal bond distances are obtained from interpolation using four points.

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References


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