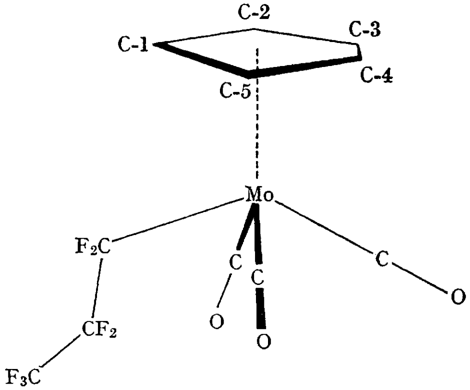
A Direct Comparison of Molybdenum–Alkyl and Molybdenum–Perfluoroalkyl Bond-lengths

By MELVYN R. CHURCHILL and JAMES P. FENNESSEY
(*Department of Chemistry, Harvard University, Cambridge, Massachusetts* 02138)

A NUMBER of explanations have been advanced to explain the thermal and aerobic stability of transition-metal fluoroalkyl derivatives.[1] Following spectroscopic evidence that this phenomenon might be the result of d_{π}–σ^* back-donation,[2] the crystal structures of a number of fluoroalkyls have been examined.[3] Although the metal–carbon distances thus obtained are shorter than those predicted for non-fluorinated alkyls, no direct comparisons of metal–carbon bond-lengths in analogous alkyl and perfluoroalkyl complexes have been reported. Since the structure and stereochemistry of π–$C_5H_5Mo(CO)_3Et$ have been accurately established[4,5] (and the molybdenum–ethyl distance found to be consistent with other measurements[4,6]), it seemed advisable to study a similar perfluoroalkyl[7] complex. A complete three-dimensional X-ray structural analysis of the perfluoropropyl complex, π–$C_5H_5Mo(CO)_3C_3F_7$, was therefore undertaken.

The molecule crystallizes in space-group $P2_1/c$ (No. 14) with $a = 8{\cdot}30$, $b = 15{\cdot}24$, $c = 11{\cdot}25$ Å, $\beta = 106°\ 15'$, $Z = 4$. Using Mo-K_{α} radiation, complete three-dimensional data ($\sin \theta_{\max} = 0{\cdot}41$) were collected with an automated diffractometer. The structure was solved by Patterson, Fourier, and least-squares refinement techniques, the final discrepancy index being $R = 10{\cdot}35\%$ for 2172 independent reflections. The Figure shows the stereochemistry to be similar to that in the corresponding ethyl complex.[4]



FIGURE

The molybdenum–perfluoropropyl linkage is $2{\cdot}282 \pm 0{\cdot}013$ Å in length indicating an Mo–C bond order of $\sim 1{\cdot}17$;[6] other bond-lengths involving the α-carbon atom are close to their expected values (C_α–F-1 = $1{\cdot}370 \pm 0{\cdot}011$, C_α–F-2 = $1{\cdot}375 \pm 0{\cdot}011$, C_α–C_β = $1{\cdot}495 \pm 0{\cdot}013$ Å). The contraction of $0{\cdot}115$ Å (*i.e.*, 9σ) from Bennett's final[5] value of $2{\cdot}397 \pm 0{\cdot}019$ Å for the molybdenum–ethyl linkage provides the first direct information on the magnitude of the contraction in metal–carbon bond-length that may be expected on fluorinating an alkyl group. It should be emphasized that, if the postulate of d_π–σ^* back-donation is correct, then the amount of overlap (and concomitant contraction in metal–carbon bond-length) will be a function of the energy separation of metal (d_π) and carbon–fluorine (σ^*) orbitals. Thus, the observed contraction of $\sim 0{\cdot}1$ Å may be characteristic of second-row transition metals, but a smaller contraction might be expected with first-row metals. The observed metal–fluoroalkyl distance of $2{\cdot}068 \pm 0{\cdot}014$ Å (average) in *cis*-$[(HCF_2{\cdot}CF_2)_2Fe(CO)_4]$[3d] is in keeping with this hypothesis.

The perfluoropropyl group is in the customary[3] staggered conformation, the M–C_α–C_β angle being 123·3°, which is significantly greater than the regular tetrahedral value of 109·5°. Other fluoroalkyls show a similar effect, corresponding angles being:

π-$C_5H_5Rh(CO)(C_2F_5)I$ [3c] 116·4°

$K_3[Co(CN)_5CF_2{\cdot}CF_2H]$ [3b] 119·7°

cis-$[(HCF_2{\cdot}CF_2)_2Fe(CO)_4]$ [3d] 121·2° (average)

(It should be noted, however, that Bennett,[5] observes a value of 120·9° for the Mo–CH_2–CH_3 angle.)

The molybdenum atom lies 1·992 Å below the planar (r.m.s. deviation 0·005 Å) π-cyclopentadienyl ring. The Mo–C distances vary systematically around the π-cyclopentadienyl ring in such a way as to conserve the approximate mirror symmetry of the molybdenum co-ordination sphere (Mo–C-1 = 2·370, Mo–C-2 = 2·348, Mo–C-3 = 2·301, Mo–C-4 = 2·312, Mo–C-5 = 2·336; each ± 0·009 Å). The greatest value is for C-1, immediately above the C_3F_7 group. This is also the case for π-$C_5H_5Mo(CO)_3C_2H_5$;[5] the same general pattern of Mo–C distances is observed in all other molecules containing π-$C_5H_5MoL_3$ groups,[8,9] and thus appears to be due to an electronic, rather than steric, effect.

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