Molecular Geometry in a π-Cycloheptatrienylmolybdenum Cation

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WE report the first crystal structure determination of a cation containing the tropylium moiety, π-cycloheptatrienylmolybdenum tricarbonyl fluoroborate [$C_7H_7Mo(CO)_3^+$ BF_4^-]. The $C_7H_7Mo(CO)_3^+$ ion exhibits a unique interaction between the tropylium ring and the molybdenum atom. The result of this interaction is an increase in the Mo–C (carbonyl) bond length relative to the corresponding bonds in neutral olefin–$Mo(CO)_3$ complexes.

The crystals are orthorhombic with $a = 16{\cdot}297 \pm 0{\cdot}002$, $b = 12{\cdot}955 \pm 0{\cdot}002$, and $c = 11{\cdot}749 \pm 0{\cdot}001$ Å. The space group was uniquely determined from the systematic absences to be *Pbca*. The density calculated for 8 molecules per unit cell is 1·91 g./cm.^{3}, in agreement with the measured value of 1·90 g./cm.^{3}. Intensity data were measured using a Datex Automated General Electric XRD-6 Diffractometer. The stationary crystal-stationary counter technique was employed to measure about 8500 reflections with $2\theta \leqslant 135°$ for copper radiation. A total of 2234 unique reflections was obtained after averaging equivalent reflections, of which 1392 were considered to be observed.

The structure was solved by locating the molybdenum atom with the aid of the Patterson Function. The light atoms were found in successive Fourier syntheses. The trial structure was refined by full-matrix least-squares methods using iosotropic and then anisotropic thermal parameters. The hydrogen atoms on the C_7 ring were included in the structure factor calculations for the final cycles but their parameters were not refined. The final reliability index was 0·050.

The tropylium ring is planar with an average C–C bond length of 1·401 Å which is typical of a delocalized system. The corresponding value for $C_7H_7VC_5H_5$[1] is 1·403 Å, in good agreement with our results. Both $C_7H_7VC_5H_5$[2] and $C_7H_7V(CO)_3$,[2] the only two compounds containing a planar C_7H_7 ring whose structures have been reported, are green. However, $C_7H_7Mo(CO)_3^+$ BF_4^- and $C_7H_7Mo(CO)_2C_5H_5$ are orange. The orange colour of the latter, in contrast to the green colour of the vanadium compounds, led King and Bisnette[3] to suggest that the C_7H_7 group was acting as a π-allyl system. However, our results suggest that colour is an unreliable indicator of geometry.

The idealized configuration about the molybdenum atom is octahedral, assuming that the tropylium ring occupies three sites. The distances from the molybdenum atom to the carbon atoms in the ring vary from 2·29 to 2·33 Å, similar to the values found in other olefin $Mo(CO)_3$ compounds.[4–6]

One surprising feature of the structure is the average Mo–C(carbonyl) distance of 2·035 Å which is appreciably longer than in other olefin–$Mo(CO)_3$ complexes. The increase in the Mo–C distance from 1·94 Å in diethylenetriaminemolybdenum tricarbonyl to 2·06 Å in molybdenum hexacarbonyl has been rationalized in terms of a decrease in π-bonding between the molybdenum and carbonyl groups.[7] A comparison of our value of 2·035 Å with the values of 1·974 Å in cycloheptatrienemolybdenum tricarbonyl,[4] 1·996 Å in azulenetricarbonylmolybdenum dimer,[5] and 1·972 Å in guaiazulenedimolybdenum hexacarbonyl[6] indicates that our Mo–C distance is definitely longer. These observations suggest that the interaction between the tropylium ion and the molybdenum atom is not typical of other metal–olefin complexes where there is increased π-bonding relative to the hexacarbonyl. Whether the decrease in the molybdenum-carbonyl π-bonding in $C_7H_7Mo(CO)_3^+$ is related to a change in the molybdenum–tropylium σ- or π-bonding can not be answered at present.

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