The Crystal and Molecular Structures of Acetylacetonatobiscarbonylrhodium(I) and of Some Fluoro-substituted Complexes

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THE syntheses and properties of a series of dicarbonyl β-diketonates of rhodium(I) and iridium(I) have recently been reported.[1] In the crystalline state these compounds show dichroic properties, suggesting the presence of a chain of weak metal–metal interactions such as have previously been reported in other d^8 systems.[2] The colours of these compounds in the solid state vary with the nature of the substituents on the co-ordinated β-diketone as well as with the transition metal.

Acetylacetonatobiscarbonylrhodium(I) crystallises from acetone as elongated plates which show an orange–green dichroism; the crystal lattice is triclinic with $a = 7{\cdot}76$, $b = 6{\cdot}52$, $c = 9{\cdot}20$ Å, $\alpha = 91°\ 5'$, $\beta = 105°\ 58'$, $\gamma = 100°\ 14'$, $Z = 2$. Three-dimensional, room-temperature, X-ray data comprising 1586 independent reflexions were collected by photographic methods and estimated visually; corrections for absorption were applied. The very weak nature of all diffraction maxima with indices $k = 2n + 1$ provided initial co-ordinates of $x = 0$, $y = 0{\cdot}25$, $z = 0$ for the rhodium atom in space group $P\bar{1}$; investigation of the images around the origin peak and around the rhodium–rhodium inversion peak in the Patterson synthesis yielded trial co-ordinates for all light atoms (excluding hydrogen atoms). Seven cycles of block-diagonal, least-squares refinement gave $R = 0{\cdot}085$, anisotropic thermal parameters being allowed for all atoms.

The molecular skeleton (Figure 1) is essentially planar (r.m.s. deviation from plane, 0·02 Å); the two rhodium–rhodium contacts are 3·27 Å ($\sigma = 0{\cdot}006$ Å) and 3·26 Å ($\sigma = 0{\cdot}006$ Å), the metal–metal vectors lying approximately normal to the mean molecular plane.

The related hexafluoro-substituted molecule, $Rh(CO)_2(CF_3{\cdot}CO)_2CH$, shows a similar molecular packing in the orthorhombic space group $Ama2$, with $a = 6{\cdot}65$, $b = 19{\cdot}17$, $c = 8{\cdot}72$ Å, $Z = 4$. The molecules lie in the crystallographic mirror plane with a rhodium–rhodium contact at a distance of 3·34 Å ($\sigma = 0{\cdot}01$ Å). The related molecule $Rh(CO)_2(CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3)$ appears to be isomorphous with $Rh(CO)_2$acac with a slightly longer unit cell b axis indicating a rhodium–rhodium contact similar to that for the hexafluoro-substituted complex. The recently reported[3] $Ir(CO)_2(C_5H_7O_2)$ is strictly isomorphous with the rhodium analogue but shows an iridium–iridium contact of 3·20 Å.

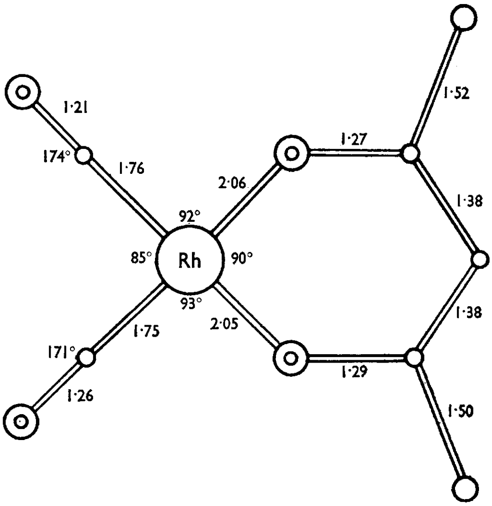

FIGURE 1. *Molecular geometry of acetylacetonatobiscarbonylrhodium*(I). Estimated standard deviations are Rh–O, 0·01; Rh–C, 0·02; C–O, 0·02; C=O, 0·03; C–C, 0·02 Å; ∠C–Rh–C, 1·2°; ∠O–Rh–C, 0·9°; ∠O–Rh–O, 0·4°; ∠Rh–C–O, 2·0°.

The increase in rhodium–rhodium distance on the introduction of trifluoromethyl substituent groups into the β-diketone ligand is a consequence of increased ligand–ligand repulsive forces, the smallest fluorine–oxygen contact being 2·45 Å. The substantially shorter metal–metal distance in $Ir(CO)_2(C_5H_7O_2)$ as compared with the rhodium analogue may be taken as an indication of a greater $d_{z^2} - p_z$ overlap in the former case, resulting in a shorter metal–metal interaction.

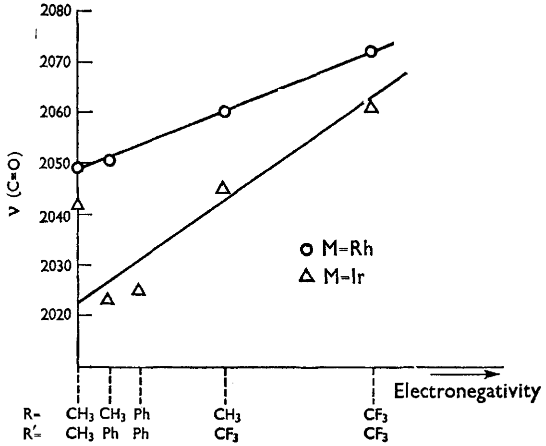

FIGURE 2. *Variation of mean carbonyl stretching frequency with substituent groups.*

This is in agreement with recent calculations[4] on the radial wave functions of 4*d* and 5*d* orbitals.

For complexes of the general formula $M(CO)_2(R{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}R')$, with M is Rh or Ir, the systematic variation of mean carbonyl infrared stretching frequency[5] (measured in n-hexane solution) with the electronegativity of groups R and R′ (Figure 2) suggests some degree of back donation of charge to the acetylacetonato-ligand to an extent which is influenced by the nature of the substituent groups. The more marked variation for the iridium series of complexes is in accord with the greater calculated overlap for $5d_\pi - 2p_\pi$ as compared with $4d_\pi - 2p_\pi$ orbitals.[4] The degree of back donation will affect the energy and size of the metal d_{z^2} and p_z orbitals and might be expected to influence slightly the strength of the metal–metal interaction in the crystalline state.

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