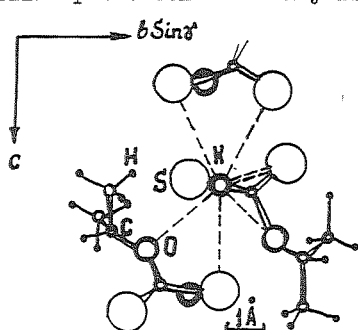


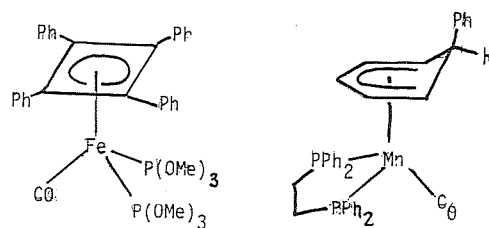
09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-28 THE CRYSTAL STRUCTURE OF ISOPROPYL XANTHATE POTASSIUM. By N.A.Frolova, S.B.Leonov, A.A.Kashaev, Irkutsk State University, Irkutsk, and V.Ch.Kravtsov, M.D.Mazus, Institute of Applied Physics, Moldavian SSR Academy of Sciences, Kishinev, USSR.

$C_4H_7KOS_2$ crystals of prismatic habitus have the following unit cell parameters: $a=6,616(4)\text{\AA}$, $b=19,337(8)\text{\AA}$, $c=12,463(5)\text{\AA}$, $\beta=94,78^\circ(8)$, $Z=8$, space group $P2_1/b$. The experimental intensities have been measured by the automatic diffractometer. The structure is solved by direct methods and refined by least-squares to $R=0,052$ for 1735 independent reflexions. The fragment of environment structure projection for K atoms is shown in the figure. K atoms occupy 2 crystallographically independent positions and form the polyhedra rather close in shape which are made up of seven S atoms and two O atoms. The investigated structure is the aggregate of $b/2$ thickness layers oriented parallel to (010). Polyhedrals of K atoms joined by common faces fill up the centre of layers but the end of

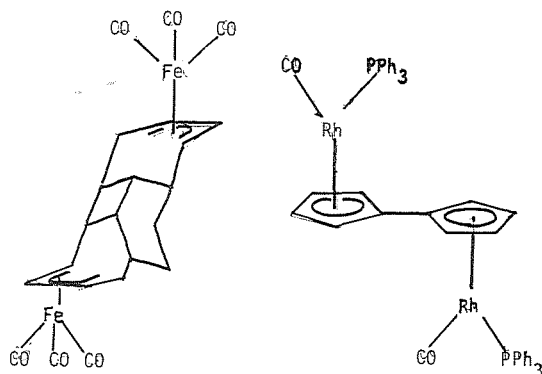


hydrocarbon radicals $-\text{CH}(\text{CH}_3)_2$ go out through the O atoms to the periphery of layers.



(1)

(2)



(3)

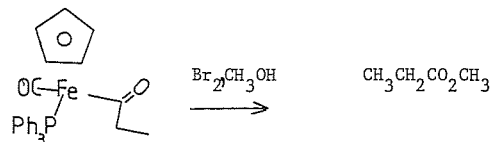
(4)

09.3-29 STRUCTURAL ORGANOMETALLIC CHEMISTRY: REDUCTION-OXIDATION EFFECTS. By N.G. Connelly, M.J. Freeman, I. Manners, A.G. Orpen, and J.B. Sheridan, Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

We report the X-ray crystal structure analyses of a series of pairs of organometallic complexes, each pair consisting of a neutral molecule and its singly or doubly oxidised cation. Both mono- and di-metal complexes of this type have been characterised (1)-(4) below. The mononuclear complexes (1) and (2) show no gross structural changes on oxidation to their respective radical monocations. The detailed changes in bond lengths may be related to the effect of removing one electron from the HOMO together with charge effects on metal-ligand bonding. For the dinuclear complexes (3) and (4) rather more spectacular geometry effects are observed on double oxidation. Thus in (3) oxidation to the (diamagnetic) dication causes carbon-carbon bond cleavage and iron-carbon bond formation. The carbon-carbon bond cleaved is the longest in a strained cyclobutane ring ($1.595(4)\text{\AA}$, c.f. others in the ring average $1.536(4)\text{\AA}$). In the dication of (3) the two carbon atoms are separated by 3.78\AA . Remarkably the C-C bond is specifically reformed on reduction of the dication by sodium amalgam. The dinuclear fulvalene complex (4) exists as the transoid isomer in the solid state with rhodium atoms on opposite sides of the fulvalene (Rh-Rh $5.662(2)\text{\AA}$). In the diamagnetic dication of (4) the rhodium atoms lie on the same side of the fulvalene group and are bonded to one another (Rh-Rh $2.930(2)\text{\AA}$).

09.3-30 STRUCTURES OF IRON COMPLEXES OF INTEREST IN SYNTHETIC ORGANIC CHEMISTRY. By Gordon Baird and Stephen Davies, The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, and Judith Bandy, Richard Jones and Keith Prout, Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD.

Transition metal acyl complexes are of interest in synthetic organic chemistry because the range of mild decarbonylation methods available leads to a variety of carbonyl compounds e.g.



Alkylation of the corresponding enolates has been shown¹ to be extremely stereoselective. We have thus undertaken the investigation of compounds Ia-c by X-ray crystallography to ascertain the cause of this stereoselectivity.