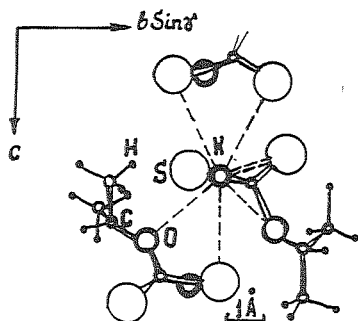


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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.

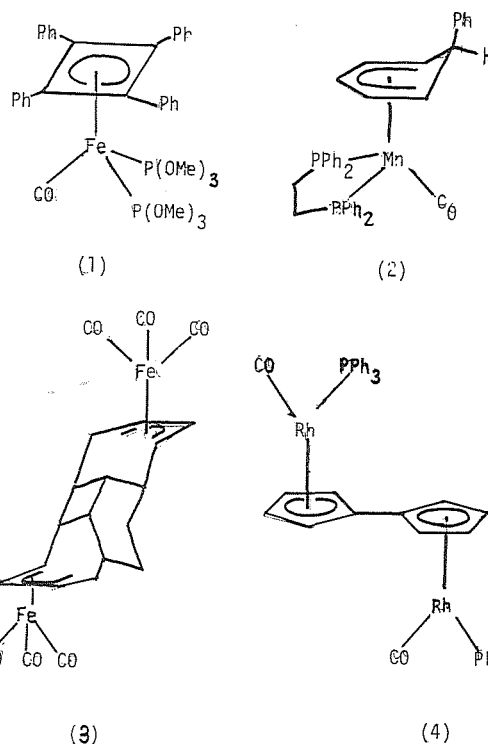
$C_4H_7KOS_2$ crystals of prismatic habitus have the following unit cell parameters: $a=6,616(4)\text{\AA}$, $b=19,337(8)\text{\AA}$, $c=12,463(5)\text{\AA}$, $\beta=94,78^\circ(8)$, $Z=8$, space group $P2_1/b$. The experimental intensities have been measured by the automatic diffractometer. The structure 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.



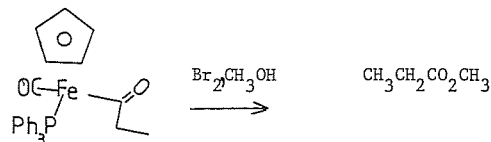
09.3-29 STRUCTURAL ORGANOMETALLIC CHEMISTRY: REDUCTION-OXIDATION EFFECTS. By N.G. Connelly, M.J. Freeman, I. Manners, A.G. Orpen, and J.B. Sheridan, Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

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 $2.930(2)\text{\AA}$).



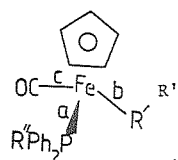
09.3-30 STRUCTURES OF IRON COMPLEXES OF INTEREST IN SYNTHETIC ORGANIC CHEMISTRY. By Gordon Baird and Stephen Davies, The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, and Judith Bandy, Richard Jones and Keith Prout, Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD.

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.

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS



R''	Ph	NEt ₂	Ph
a	2.193(1)	2.190(1)	2.205(1) ^o
b	1.964(3)	1.972(3)	1.974(5)
c	1.733(3)	1.732(3)	1.729(5)
ab	89.3(1)	89.0(1)	92.0(2) ^o
ac	92.1(1)	94.3(1)	91.7(2)
bc	94.8(1)	95.4(1)	93.7(2)

Since the inter-bond angles at the iron atom are close to 90° the coordination at iron is better described as octahedral not tetrahedral. The relative configuration of the new chiral centre in Ia and Ib, and the prochiral centre in Ic is established. The carbon monoxide ligand is in each compound *anti* to the carbon oxygen bond. If this *anti* conformation is preferred in the enolate (R' = -OC=CHR) the approach of an electrophile will occur on the face of the enolate which is not shielded by a phenyl group of the phosphine ligand thus determining the stereochemistry of the product.

References

1. G. J. Baird, J. A. Bandy, S. G. Davies and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 1202.

09.4-1 CRYSTAL AND MOLECULAR STRUCTURE OF DICYANO-COBYRINIC ACID HEPTAMETHYL ESTER.

by J.C.A. Boeyens, A.J. Markwell and M.S. Shaikjee
Department of Chemistry, University of the Witwatersrand
Johannesburg, Republic of South Africa.

The crystal and molecular structure of the vitamin B₁₂ derivative, dicyano-cobyrinic acid heptamethyl ester, has been determined. The structure was solved (4270 independent reflections measured on a diffractometer) using standard Fourier methods, with initial phasing using the cobalt atom, to an R-factor of 0.1068. The space group is P1 with Z = 2; unit cell dimensions, a = 16.332, b = 13.252, c = 14.475 Å; α = 90.0, β = 109.75, and γ = 90.0°. The two cyanide ligands are bonded in a linear fashion to the cobalt, the one in the 'lower' position being H-bonded to an isopropanol molecule. There are no significant differences between the two crystallographically independent molecules, except for their orientations in the unit cell.

09.4-2 DEVELOPMENT OF KNOWLEDGE OF THE LIGAND TRANS-STRENGTHENING. By L.A. Aslanov, Chemistry Department, Moscow State University, Moscow, USSR.

In development of the earlier investigation (O.A. Reutov et al., *Koordinatsionnaya Khimiya* (1982) 8, 1161 (Russ.)) the ligand trans-strengthening in octahedral complexes of tin (IV) was studied by the X-ray crystallography methods. This type of interaction is apparent in iodine complexes, e.g. EtSnI₃. 2HMPTA (i) (HMPTA=hexamethylphosphotriamid). It can be described as a shortening of the Sn-I_{trans} interatomic distance 2,634(2) Å in trans-position to Et-group. This distance is shorter than Sn-I in SnI₄.Dipy (ii), SnI₄.2TPPO (iii) (Dipy=2,2'-dipyridyl, TPPO=triphenylphosphin-oxide) 2,782(2)-2,819(2) Å, and even shorter than Sn-I in SnI₄ 2,69(2) Å (F.Meller, I.Fan-kuchen, *Acta Cryst.* (1955) 8, 343). Such anomalous shortening of Sn-I_{trans} inspite of the increase of coordination number from 4 to 6 is found first. It can be explained by the electron-donating Et-ligand influence and is observed simultaneously with displacement of the equatorial ligands from equatorial plane to I_{trans}. Cis-weakening of Sn-I_{cis} bonds in (i) in comparison with Sn-I in (ii) and (iii) is relatively smaller (3,8%) than trans-strengthening (5,8%). These facts show that trans-strengthening is a special phenomenon, which determines together with cis-weakening the structures of octahedral tin(IV) complexes. The single crystals without statistical distribution of alkyl groups and halogen atoms (L.A. Aslanov et al., *Organometal. Chem.* (1978) 144, 39) were grown for compounds Alk_nSnHal_{4-n}. 2L (Alk=Et, Bu; n=0,1; Hal=Cl, Br; L=TPPO, HMPTA etc.). The Sn-Cl bond distances give no information about trans-strengthening, but the trans-strengthening was found by IR- and Raman - spectroscopy both in chlorine and bromine complexes. The shortening of Sn-Br_{trans} distances in bromine complexes is smaller in comparison with Sn-I_{trans} bonds in iodine complexes. The Alk Sn Hal₃. 2L (L=N-donor ligands) compounds have a structural peculiarity: nitrogen atom is situated in trans-position to Alk-group without shortening of the Sn-N bond; cis-weakening with Hal=I becomes moderate. The (Alk Sn Cl₅)²⁻ anion complexes have the shortest Sn-Cl bond in trans-position to Alk-group, but this bond is not shorter than one in (Sn Cl₆)²⁻. Investigation of the (Alk Sn Hal₅)²⁻ (Hal=Br, I) complexes is in progress.