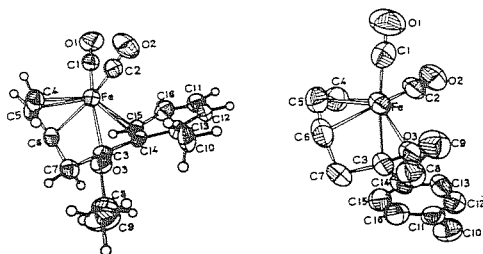


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

I and II respectively.

The results of structure analyses show that: In reaction one π bond of each butadiene molecule has been opened with the aid of iron medium so as to cause carbon atom C7 to form a new bond with the "carbene" atom C3 and leave the other three carbon atoms C4, C5 and C6 of butadiene bonded to Fe atom by p- π molecular orbital. Both molecular structures satisfy 18-electron rule evidently, but in somewhat different and interesting ways. Very fascinatingly, on the basis of the bond distances and group orientations, it may be established that in molecule I the bonded π -molecular orbital composed by C14 and C15 in benzenering which exhibits certain character of Kekule structure, should overlap with the orbital of Fe, whereas in molecule II, the atom O3 of ethoxy coordinates to iron instead, completing the full valence shell of metal atom.



(I)

(II)

to indicate Li-Li bonding. The lithium atoms are also symmetrically above and below the plane (± 0.80 Å) of the enamine functional groups. This molecular structure corresponds closely to the minimum energy configuration calculated by *ab initio* methods for the lithium enolate of acetaldehyde, thus providing the first experimental proof of this prediction.¹ This structure is totally dissimilar to the x-ray structures of THF-solvated lithium enolates.²

The molecular structure of (I) will be presented along with other organolithium derivatives that have been widely used as reactive intermediates in synthetic organic chemistry.

¹T.J.Lynch, M.Newcomb, D.E.Bergbreiter and M.B.Hall, *J.Org.Chem.*, 1980, 45, 5005.

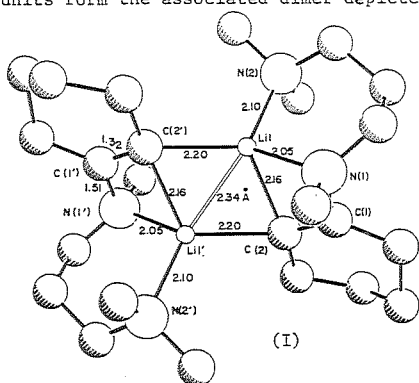
²R.Amstutz, W.B.Schweizer, D.Seebach and J.D.Dunitz, *Helv.Chem.Acta*, 1981, 64, 2617.

09.3-3 ORGANOLITHIUM DERIVATIVES - REACTIVE INTERMEDIATES IN ORGANIC SYNTHESIS: A CRYSTALLOGRAPHIC INVESTIGATION.

By Paul G. Williard, Dept. of Chemistry, Brown Univ., Providence, Rhode Island 02912, U.S.A.

N-(2-Lithiocyclohexenyl)-N,N',N'-trimethyl-1,3-propanediamine (I) is a stable solid. This compound is important as the functional equivalent of the enolate anion of cyclohexanone. The crystallographic asymmetric unit of (I) is a monomer of molecular formula $C_{12}H_{22}LiN_2$.

The asymmetric units of (I) are sufficiently close to crystallographic inversion centers so that two asymmetric units form the associated dimer depicted.



(I)

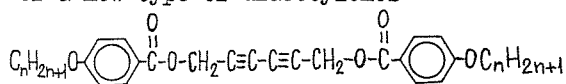
The doubly bridging sp^2 -carbons, C(2) and C(2'), are unexceptional and have an analogy in the structures of several aryl lithium derivatives. However, the lithium atoms lie close enough together (2.34 Å)

09.3-4 SOLID STATE POLYMERIZATION OF

DIACETYLENES. By V.E.Shklover, Yu.T.Struchkov (Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, USSR), I.A.Bagirov, I.I.Konstantionov, Yu.B.Amerik (Topchiev Institute of Petrochemistry of the USSR Academy of Sciences, Moscow, USSR)

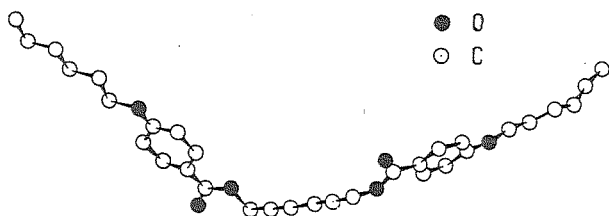
At present there are crystal structural data on 24 diacetylenes, of which 17 are polymerizable in solid state, and on about 6 polydiacetylenes, formed via the solid state polymerization of corresponding diacetylenes, proceeding (except for one case) by the shearing mechanism, defined by the packing geometry parameters S_I and γ_I (G.Wegner, *Chemistry and Physics of One-Dimensional Metals*, Plenum, New York, 1977, p.297; R.H.Baughman, *J.Pol.Sci.-Phys.* (1974) 12, 1511).

We carried out a physico-chemical study of a new type of diacetylenes



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where $n=5$ (I), 6 (II) and 7 (III). An X-ray study of I and II was also performed. In crystal I polymerizes very rapidly (stack packing, $S_I=3.36 \text{ \AA}$, $\delta_I=42.4^\circ$), II polymerizes slowly (stack packing, two types of intermolecular contacts between diacetylene rods; $S_{II}=3.81$ and 4.63 \AA , $\delta_{II}=67.5$ and 63.4°), III does not polymerize at all. The molecules I and II have different conformations (trans-planar for I, skew for II) possibly resulting in the different structure of stacks of diacetylene rods in their crystals and consequently in a different tendency to the solid state polymerization.



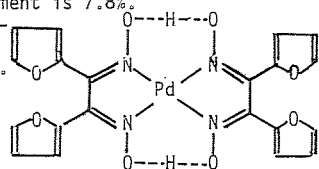
Molecular structure of II

09.3-5 SHORT HYDROGEN-BONDED, COLUMN-STACKED STRUCTURE OF BIS (ALPHA-FURIL DIOXIMATE) PALLADIUM(II).

By M. Sakhawat Hussain, Department of Chemistry, University of Petroleum and Minerals, Dharam, Saudi Arabia

The single crystal X-ray structure of the title compound was done due to its importance having electrical conduction properties and exhibiting intramolecular short hydrogen bond. The compound crystallizes in the orthorhombic space group $Pnab$ with $a=6.930(3)$, $b=14.286(2)$ and $c=19.837 \text{ \AA}$. The structure was solved using intensity data collected on an Enraf-Nonius CAD4 diffractometer and SDP82 in TAXRAY 230 system. The final R value at the present stage of refinement is 7.8%.

The most important features of the structure are shown in the figure. The central metal atom has planar geometry with oxime oxygen atoms forming an intramolecular hydrogen bond. The complex molecules are stacked above one another along the a axis with adjacent molecules rotated by 90 degrees with respect to each other. The column stack structure in this compound is similar to the structures of chelates exhibiting one-dimensional electrical conduction properties. The oxygen atoms of the furane moieties in the complex are oriented at an angle of 47 degrees and are at a non-bonded distance of 2.66 \text{ \AA}. The Pd-Pd distance of 3.465(4) \text{ \AA} is similar to the palladium complexes having desirable conduction properties. The infrared spectra and the chemical shifts of the bridged proton were studied and efforts were made to find some co-relations between the shifts in infrared absorptions and chemical shifts and the O-H-O distance. The infrared spectra of several other vic-dioximates and alpha-amine dioximates will be discussed and compared with the title compound.

09.3-6 THE MOLECULAR STRUCTURE OF BIS(η^5 -CYCLOPENTADIENYL) BIS(ETHYLTHIOLATO)TITANIUM(IV), (η^5 -C₅H₅)₂Ti(SC₂H₅)₂. By M.A.A.F. de C.T. Carrondo and C.F. Frazao, Centro de Quimica Estrutural, Complexo I, I.S.T., 1000 Lisboa, Portugal.

The molecular structures of complexes of the type $[M(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2]$ ($M=\text{Mo}, \text{Ti}$, $\text{L}=\text{polyatomic ligand}$) have been published recently (Carrondo and Jeffrey, *Acta Cryst.* (1983), **C39**, 42; Carrondo and Domingos, *J. Organomet. Chem.* (1983), **253**, 53; Carrondo, Matias and Jeffrey, *Acta Cryst.* in the press).

We are now reporting preliminary results for the structure analysis of the title complex. A single crystal was used to collect 1413 hkl intensities on a CAD-4 X-ray diffractometer (offered to the Coimbra University by the Deutscher Akademischer Austauschdienst and the German Agency for Technical Cooperation); $M_r=300.34$, monoclinic, $P2_1/c$, $a=9.286(3)$, $b=20.583(8)$, $c=8.345(6) \text{ \AA}$, $\beta=112.18(4)^\circ$, $V=1477.0 \text{ \AA}^3$, $\lambda(\text{Ag K}\alpha)=0.5609 \text{ \AA}$. The structure was solved with SHELX to an $R_w=0.060$. The Ti coordination is a distorted tetrahedron formed by the two S atoms of the ethylthiolato ligands and the ring normals to the cyclopentadienyl rings. The Ti atom is at an average distance from the Cp rings of 2.091(15) \text{ \AA} and the angle between the ring normals is 131.2(2)^\circ. The Ti-S(1) and Ti-S(2) bond lengths are 2.388(5) and 2.387(5) \text{ \AA} and the S(1)-Ti-S(2) bond angle is 93.5(2)^\circ. Equivalent values for these parameters were found for the reported structure of (η^5 -C₅H₅)₂Ti(SCH₃)₂ (Carrondo and Jeffrey quoted above).

The final results of this study will be published in a full paper together with theoretical calculations (EHMO) and thermochemical studies (Ti-S bond energy).

09.3-7 STRUCTURAL PARAMETERS OF SULPHUR AND SELENIUM-CONTAINING TRANSITION METAL COMPLEXES.

By G.J. Kruger and H.G. Raubenheimer, Chemistry Dept., Rand Afrikaans University, Box 524, Johannesburg 2000, South Africa

The crystal structures of several novel metal-coordinated S and Se-containing transition metal complexes were determined as part of a research programme concerned with the synthesis of organic compounds that are difficult to obtain, prepare, or stabilize. Group VI transition metal carbonyls were used as starting materials during metal template syntheses.

Among the complexes whose structures are reported are: the first thioaldehyde reported,

$[\text{Cr}(\text{CO})_5\{\text{S}=\text{CHCH}=\text{C}(\text{SEt})_2\}]$; the 1,2-dithiole-3-thione, $[\text{W}(\text{CO})_5\{\text{S}=\text{C}-\text{S}-\text{S}-\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$; and the novel selenocarbene, $[\text{W}(\text{CO})_5\{\text{C}=\text{Se}-\text{Se}-\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$.

The comparable S-S and Se-Se bonds in the last two complexes have lengths of 2.056(8) and 2.295(2) \text{ \AA} respectively.