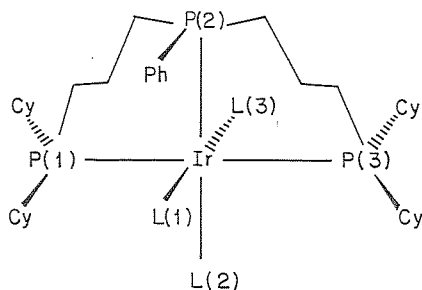


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-13 CRYSTAL STRUCTURES OF DIHYDRIDE AND TRIHYDRIDE COMPLEXES OF $\text{Ir(III)((C}_6\text{H}_5)_2\text{P(CH}_2\text{CH}_2\text{CH}_2\text{-P(C}_6\text{H}_{11})_2)_2)_2\text{L}_3$. By Dennis J. Kountz, Chihae Yang and Devon W. Meek, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

The title compounds are the first crystal structures of the tridentate ligand $(\text{C}_6\text{H}_5)_2\text{P(CH}_2\text{CH}_2\text{CH}_2\text{-P(C}_6\text{H}_{11})_2)_2$, Cyttp. The dihydride $\text{Ir(Cyttp)(H)}_2\text{Cl}$ (I) crystallizes in the space group $\text{P}\bar{1}$ with $Z = 2$ and unit cell dimensions $a = 12.632(2)$, $b = 13.110(2)$, $c = 11.120(1)$, $\alpha = 97.65(1)$, $\beta = 92.02(1)$ and $\gamma = 78.58(1)$ at 159 K. $R(F) = 0.040$ based on 7945 reflections with $F_o^2 > 0$ ($\sin\theta/\lambda \leq 0.650 \text{ \AA}^{-1}$ using $\text{MoK}\alpha$ radiation). The trihydridic $\text{Ir(Cyttp)(H)}_3\cdot\text{CH}_3\text{CH}_2\text{OH}$ (II) crystallizes in the space group $\text{P2}_1/\text{m}$ with $Z = 2$ and unit cell dimensions $a = 10.737(1)$, $b = 18.484(3)$, $c = 11.155(1)$ and $\beta = 120.297(9)$ at 150 K. $R(F) = 0.052$ based on 6810 reflections with $F_o^2 > 0$ ($\sin\theta/\lambda \leq 0.756 \text{ \AA}^{-1}$ using $\text{MoK}\alpha$ radiation). $\text{L}(1) = \text{L}(2) = \text{H}$ for compounds I and II. $\text{L}(3) = \text{Cl}$ and H for compounds I and II respectively.



Atoms	Compound I	Compound II
Ir-P(1)	2.298(1) Å	2.2774(9) Å
Ir-P(2)	2.309(1) Å	2.2763(9) Å
Ir-P(3)	2.305(1) Å	2.2774(9) Å
Ir-L(1)	1.63 Å	1.77 Å
Ir-L(2)	1.70(5) Å	1.58 Å
Ir-L(3)	2.528(1)°	1.71 Å
P(1)-Ir-P(2)	90.52(4)°	95.89(2)°
P(1)-Ir-P(3)	170.67(4)°	161.82(3)°
P(2)-Ir-P(3)	92.97(4)°	95.89(2)°

Surprisingly, $\text{L}(3)$ appears to be relatively unreactive. $\text{L}(2)$ is readily attacked by electrophilic reagents, however $\text{L}(1)$ does not react with an excess of the electrophile. Both compounds undergo HD exchange with common organic solvents. The ^1H , ^2H and ^{31}P NMR spectral data will be discussed in terms of the steric and geometric requirements of the Cyttp ligand.

09.3-14 THE STRUCTURE OF LITHIUMFLUORENIDE-A LITHIUM SANDWICH-COMPLEX. By H.-J. Schmidt and D. Rewicki, Institut für Organische Chemie der Freien Universität Berlin, West-Germany.

Lithium organic compounds with delocalized carbanions are mostly found as amin or ether contact-ion-pair complexes. In these structures the pi-carbanion and the basic nitrogen or oxygen centres are bonded to lithium in a trigonal-planar arrangement, in contrast to the sandwich structure observed here.

We succeeded in getting red crystals of the air-sensitive Lithium-fluorenid without the addition of a stabilizing, heteroatom containing base. The compound crystallizes in the monoclinic space-group $\text{P2}_1/\text{a}$ with dimensions

$a = 13.843(2)$, $b = 11.323(2)$, $c = 6.221(2) \text{ \AA}$

and $\beta = 110.51(2)^\circ$. The crystal lattice is composed of two isolated units of the lithium sandwich-complex per cell. The fluorenyl-anions are orientated anti-parallel 3.92 \AA from each

other. The lithium atoms are found 1.96 \AA above the six-membered ring plane. (Fig. 1) However, the distances of the lithium to the carbon atoms of the six-membered ring are not equal. To the "outer" atoms $\text{C}(2)$, $\text{C}(3)$, $\text{C}(4)$ and $\text{C}(5)$ ' $\text{C}(6)'$, $\text{C}(7)'$ they are between $2.339(8)$ and

$2.390(6) \text{ \AA}$ and thus significantly shorter than to the "inner" atoms $\text{C}(8)$, $\text{C}(12)$, $\text{C}(13)$ and $\text{C}(1)'$, $\text{C}(10)'$, $\text{C}(11)'$. These range between

$2.423(6)$ and $2.499(6) \text{ \AA}$.

In the structure presented here the lithium atom does not approach the carbon atom with the highest charge density which would be $\text{C}(9)$ according to MO-calculations. In accordance with the results of the structure investigation of Lithium-7bH-indeno-(1,2,3-jk)fluorenone (Bladauski, Dietrich, Hecht und Rewicki, *Angew. Chem.* (1977) **89**, 490), we may conclude that in the absence of heteroatom containing bases the structure of a lithium organic compound with delocalized carbanions is rather determined by polyhapto bonding than by electrostatical interactions. Results of CNDO calculations will be discussed.

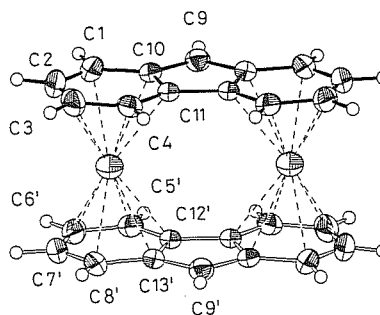


Fig. 1