

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-10 STRUCTURAL PROPERTIES OF $R_2PCH_2PR_2$ -BRIDGED COMPLEXES OF PALLADIUM AND PLATINUM. By Lj.

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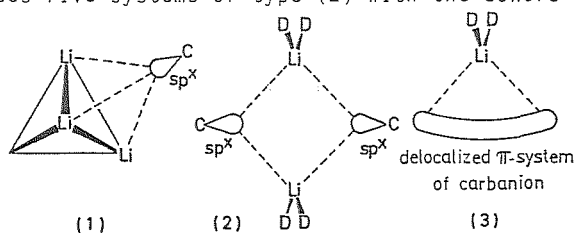
Complexes of palladium and platinum stabilised by bridging $R_2PCH_2PR_2$ ligands display diverse and often novel structural properties, including several modes of metal-metal interactions. Their molecular structures are systematically studied in our laboratory by diffraction techniques. The object is to investigate the role of the $R_2PCH_2PR_2$ (R = Ph or Me) ligands in promoting rich and versatile reactivity of these complexes and elucidate the interplay between electronic and steric demands of the metal centres, steric flexibility of the bridging phosphines and conformational changes of the $M_2P_2C_n$ dimetallacycles. New results on homo- and hetero-bimetallic and poly-metallic complexes in which the oxidation state of the metal atom changes from 0 to +4 will be shown.

09.3-11 NEW LITHIUM ORGANIC STRUCTURES AND THEIR INTERPRETATION. H. Dietrich^a, W. Mahdi^a, P. v. R. Schleyer^b, W. Neugebauer^b, T. Clark^b, D. Wilhelm^b, G. Boche^c and H. Etzrodt^c

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The electronegativity difference of Li and C does not suffice to suppress the involvement of the Li 2s and 2p orbitals in a C-Li bond. The resulting electron deficient compounds are often oligomers. For tetramer methyl lithium E. Weiss and E. A. C. Lucken (J. Organometal. Chem. (1964)2,197) have proposed that the tetramer is stabilized by 4-centre bonds (1) ($x=3$) which is supported by bonding density maxima found in tetramer ethyl lithium (H. Dietrich, J. Organometal. Chem. (1981)205,291).

The multicentre bonding in our present series of unsaturated organo-lithium structures includes five systems of type (2) with the donors D



being hetero-atoms (N,O) or π -bonds, and six systems of type (3) with D = 1,2-bis(dimethylamino)ethane.

(2) is analogous to the diborane molecule, i.e. it is stabilized by two 3-centre bonds, for which localized carbanion orbitals ($x=2$ or 3) must be available. One of these complexes has the point symmetry 2, another one approximately 2 and the remaining three 1. Two of the structures contain allenyl groups which offer a sp^2 orbital for the 3-centre bond, while their π -system acts as a donor D.

If the carbanion charge is π -delocalized, type (2) structures are not possible. Instead the DDLi moiety can be π -bonded to the carbanion in the fashion (3). The position of this π -bonding on the carbanion surface shows where the Li finds sufficient charge and optimal overlap. This is not only a function of charge delocalization but also of conformation of the anion. The six systems of type (3) contain dianions. Thus, a second DDLi group is π -bonded at the opposite π -surface of the dianion. Three of the structures have an approximate symmetry 2.

All phenyl groups involved show a characteristic deformation pattern of the bond angles within the ring suggesting an increased weight of a p-quinoid resonance structure. This is plausible, since the C-C bond connecting the ring to the chain has increased bond order and some of the charge is transferred to the (peripheral) p-position.

09.3-12 NEUTRON DIFFRACTION STUDY OF THE C-H-Ti INTERACTION IN $TiMeCl_3(dmpe)$.* A. J. Schultz and J. M. Williams, Argonne National Laboratory, Argonne, Illinois 60439, USA; T. F. Koetzle, Brookhaven National Laboratory, Upton, New York 11973, USA; Z. Dawoodi, M. L. H. Green and K. Prout, University of Oxford, Oxford OX1 3QR, U.K.

Previous neutron diffraction studies using conventional and time-of-flight techniques have demonstrated the existence of stable 3-center, 2-electron C-H-metal bonds in cases where the carbon atom is not directly bonded to the metal (Schultz, et al., Science (1983), 220, 197). For interactions involving α -carbon and α -hydrogen atoms in Ta-neopentylidene complexes (Schultz, Brown, Williams and Schrock, J. Amer. Chem. Soc. (1981), 103, 169), viz., $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ and $Ta(CHCMe_3)(C_5Mes)(C_2H_4)(PMe_3)$, the Ta-C $_{\alpha}$ -C $_{\beta}$ angles approach 180°, the Ta-C $_{\alpha}$ -H $_{\alpha}$ angles are less than 90° and the C $_{\alpha}$ -H $_{\alpha}$ bonds are elongated (1.13Å). These interactions probably involve the 2 electrons in the C $_{\alpha}$ -H $_{\alpha}$ bond and a metal d π -orbital. Two common features of the Ta-neopentylidene structures are the presence of only one α -hydrogen atom and the absence of β -hydrogen atoms. We have now collected single crystal neutron diffraction data at the Brookhaven HFBR on the title compound at 20 K. A previous x-ray study (Dawoodi, Green, Mtetwa and Prout, J. Chem. Soc., Chem. Commun. (1982), 1410) indicated an interaction involving one of the three α -hydrogen atoms on the methyl ligand. The results of an analysis of the low temperature neutron data will be described in detail.

*Me = CH₃; dmpe = Me₂PCH₂CH₂PMe₂.
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