09.3-10 STRUCTURAL PROPERTIES OF R₂PCH₂PR₂-BRIDGED COMPLEXES OF PALLADIUM AND PLATINUM. By Li. Pamajovíc-Huir and K.W. Huir, Department of Chemistry, University of Glasgow, Gluegow G12 8Q, U.K.

Complexes of palladium and platinum stabilized by bridging R₂PCH₂PR₂ 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 R₂PCH₂PR₂ (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 R₂Zn₂ dimetallacycles. New results on homo- and hetero-dimetallic and poly-metallic complexes in which the oxidation state of the metal atom changes from 0 to +4 will be shown.


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), 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 β-bonds, and six systems of type (3) with D = 1,2-bis(dimethyl-amino)ethene.


Previous neutron diffraction studies using conventional and time-of-flight techniques have demonstrated the existence of stable 3-center, 2-electron C-H-titanium 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 Ti-neopentylidene complexes (Schultz, Brown, Williams and Schrock, J. Amer. Chem. Soc. (1981), 103, 160, v-iz., (Ta(CHOCH)(PMe)Cl)2 and Ta(CHOCH)(PMe)Cl) (PMe), the Ta-C-α angles approach 180°, the Ta-C-H angles are less than 90°, and the C-H bonds are elongated (1.13A). These interactions probably involve the C-H bonds in the C₂H₄ bond and a metal 3d-orbital. Two common features of the Ta-neopentylidene structures are the presence of only one α-hydrogen atom and the absence of α-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, Mtewa 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; Work supported in part by The U.S. Department of Energy.