Letter

On the Molecular Structure and Bonding in Germanocenes. The Molecular Structure of Bis(pentamethylcyclopentadienyl)germanium; a Retraction

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In 1980 we published the results of a gas electron diffraction investigation of decamethylgermanocene, $(\eta\text{-}C_5Me_5)_2Ge$.[1] The mean $Ge-C$ bond distance was reported to be about 2.32 Å. In this letter we first present the preliminary results of a similar investigation of 1,1′-dimethylgermanocene, $(\eta\text{-}C_5H_4Me)_2Ge$, where the mean $Ge-C$ bond distance is found to be about 0.2 Å longer. Secondly, we describe the results of *ab initio* molecular orbital calculations on $(\eta\text{-}C_5H_5)_2Ge$ and $(\eta\text{-}C_5Me_5)_2Ge$ which give optimum $Ge-C$ bond distances of 2.63 and 2.59 Å, respectively. Finally we present analytical results which show that the reported structure of $(C_5Me_5)_2Ge$ to be invalid, and suggest that the sample used consisted of the previously unknown compound $(C_5Me_5)GeCl$.

The sample of $(C_5H_4Me)_2Ge$ was prepared from GeI_2 and $K(C_5H_4Me)$ and purified by repeated extractions as described by Stobart *et al.*[2] It consisted of a yellow viscous oil. The electron diffraction pattern was recorded with reservoir and nozzle temperatures of about 90 °C. After completion of the electron diffraction experiments the reservoir was found to contain a deep yellow to orange solid residue which we believe to consist partly of polymerization products[2,3] and partly of non-volatile impurities. The electron diffraction

pattern was consistent from plate to plate and thus offered no indication for the presence of volatile impurities.

The electron diffraction data were found to be consistent with an angular sandwich structure similar to those found for $(C_5H_5)_2Sn$ and $(C_5H_5)_2Pb$ in the gas phase[4] and for $(C_5H_5)_2Sn$,[5] $(C_5Me_5)_2Sn$[6] and $(C_5Me_5)_2Pb$[5] in the solid phase. The mean $Ge-C$ bond distance was found to be 2.53(2) Å, much longer than that reported for $(C_5Me_5)_2Ge$, 2.322(6) Å.[1] In the latter compound the ligand rings were reported to be parallel or nearly parallel, in $(C_5H_4Me)_2Ge$ the angle between the ring planes is found to be 35(10)°.

The $M-Cl$ bond distances of monomeric gaseous $PbCl_2$,[7] $SnCl_2$[8] and $GeCl_2$[9] are 2.441(1), 2.347(7) and 2.184(4) Å, respectively, indicating that the bonding radius of Pb(II) is about 0.09 Å greater than that of Sn(II) which in turn is about 0.16 Å greater than that of Ge(II). Since the mean $M-C$ bond distances in gaseous $(C_5H_5)_2Pb$ and $(C_5H_5)_2Sn$ are 2.778(5) and 2.706(8) Å, respectively, the mean $Ge-C$ bond distance of 2.53 Å found in $(C_5H_4Me)_2Ge$ appears normal, while that reported for $(C_5Me_5)_2Ge$ appears abnormally short. The large difference is also at variance with results for $(C_5Me_5)_2Sn$,[6] $(C_5Me_5)_2Fe$[10] and $(C_5Me_5)_2Co$[10] which all have bond distances differing from those of the unsubstituted metallocenes by less than 0.02 Å.

We therefore decided to carry out *ab initio* molecular orbital calculations on $(C_5H_5)_2Ge$ and $(C_5Me_5)_2Ge$ to see whether the large difference between the $Ge-C$ bond distances in the two compounds could be reproduced and explained. The calculations were carried out with a double-zeta basis set. The molecular symmetries were assumed to be D_{5h} and the ligand geometries kept constant while the metal-ring distance was varied. Similar calculations on another main group metallocene, $(C_5H_5)_2Mg$, yield an optimum $Mg-C$ bond distance which is 0.06 Å greater than the experimental.[11]

Calculations with a valence shell electron configuration equal to that found for $(C_5H_5)_2Sn$,[6] gave results in accordance with the *aufbau* principle and was assumed to represent the ground state. The optimum $Ge-C$ bond distance was found to be 2.63 Å in $(C_5H_5)_2Ge$ and 2.59 Å in $(C_5Me_5)_2Ge$.

Since it is known that $(C_5Me_5)_2Mn$ is in a

different electronic state from $(C_5H_5)_2Mn$ and the Mn–C distance consequently 0.25 Å shorter,[10] we also carried out calculations on some alternative electron configurations. But these turned out to yield much higher energies and longer Ge–C bond distances than the ground state. In conclusion, the *ab initio* calculations provided no support for the existence of very different Ge–C bond distances in germanocenes, and increased our suspicion that the reported structure of $(C_5Me_5)_2Ge$ was incorrect.

The sample of $(C_5Me_5)_2Ge$ had been synthesized from $GeCl_2$ and $Li(C_5Me_5)$ and purified by recrystallization as described by Jutzi *et al.*[6] It consisted of pale yellow crystals which melted at 90 to 94 °C.[1] The electron diffraction data were recorded with reservoir and nozzle temperatures of about 140 °C. After completion of the experiment no residue remained in the reservoir, and the diffraction pattern was consistent from plate to plate. In sum: the sample appeared in every way to consist of *one* pure compound.

Only after the completion of the molecular orbital calculations did it occur to us that the reaction between $GeCl_2$ and $Li(C_5Me_5)$ might have been incomplete, and that our sample might have contained significant amounts of $(C_5Me_5)GeCl$. This compound has not been mentioned in the literature, but the analogous compound (η-$C_5H_5)SnCl$ is known, and the crystal structure has been determined by Noltes *et al.*[12] In this compound the mean Sn–C bond distance is about 0.1 Å shorter than in $(C_5H_5)_2Sn$ and the Sn–Cl bond distance about 0.3 Å longer than in $SnCl_2$: Comparison suggests that both the Ge–C and Ge–Cl bond distances in $(C_5Me_5)GeCl$ may be around 2.3 Å.

Neutron activation analysis has now shown that the sample used in our study of $(C_5Me_5)_2Ge$ contained stoichiometric amounts of Cl. Standardization against a sample of $GeCl_4$ shows that the Cl to Ge molar ratio is 1.00 ± 0.02. *The reported structure of $(C_5Me_5)_2Ge$ is therefore invalid.* We now intend to investigate the reaction between $GeCl_2$ and $Li(C_5Me_5)$ more closely and hope to be able to report results in the near future.

Note added in proof. Elemental analysis of the sample by Ilse Beetz, Kronach, West Germany, has given the following results: 49.52 % C, 6.21 % H, 14.51 % Cl. Calculated for $C_{10}H_{15}GeCl$: 49.37 % C, 6.22 % H and 14.57 % Cl.

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