

The Molecular Structure of Di- μ -bromobis- π -cycloheptenyldipalladium

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THE increasing interest in the structural details of the co-ordination of allyl groups to metal atoms,^{1,2} together with certain unusual features in the n.m.r. spectrum of the dimer of cycloheptenyl-palladium bromide (I) prompted us to determine the crystal structure of this compound. In the n.m.r. spectrum of (I),³ the central proton of the allylic group appears at a higher τ value, 5.2, than do the other two protons of the allylic group, 4.96.

This is the reverse of the order usually observed for co-ordinated allyl groups,⁴ and, in particular, the reverse of the order found for the dimeric cyclohexenyl- and cyclo-octenyl-palladium bromide analogues.³

The compound (I), di- μ -bromobis- π -cycloheptenyldipalladium, prepared³ by the method of Dent, Long, and Wilkinson,⁵ crystallizes in the monoclinic system, space group $P2_1/c$, $a = 11.34$,

$b = 7.32$, $c = 20.18$ Å, $\beta = 102.2^\circ$, $U = 1677$ Å³, $D_m = 2.22$ (by flotation), $Z = 4$ (dimers), $D_c = 2.21$, $M = 562.9$, $F(000) = 1072$. A Picker automatic diffractometer was used to collect intensity data; 2208 independent reflections with amplitudes greater than five electrons were used for the refinement. The present R value, calculated with anisotropic temperature factors for the palladium, bromine, and carbon atoms but neglecting any contributions from hydrogen atoms, is 0.074. The estimated standard deviations of bond distances are Pd–Br 0.005, Pd–C 0.02, and C–C 0.03 Å.

The dimer, one molecule of which forms the crystallographic asymmetric unit, is illustrated in Figure 1. The molecule is bent about the halogen

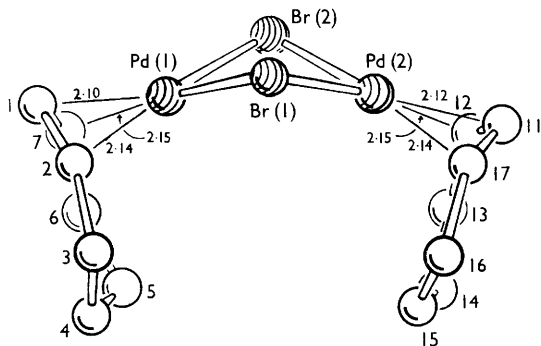


FIGURE 1. The molecule when viewed along a direction close to the Br(1)–Br(2) axis.

bridge, the dihedral angle between the planes Br(1)–Pd(1)–Br(2) and Br(1)–Pd(2)–Br(1) being 139° . The allyl groups are arranged "syn" relative to this bridge [the two allyl groups are described as "syn" if the internal bisectors of the angles C(7)–C(1)–C(2) and C(17)–C(11)–C(12) make, with the Pd–Pd line, a torsion angle that lies in the range -90° through 0° to $+90^\circ$]. In both these respects the compound (I) resembles π -1,3-dimethylallylpalladium chloride dimer.² In contrast, the dimers of π -2-methylallylpalladium chloride,¹ of π -1,1,3,3-tetramethylallylpalladium chloride,¹ and of π -allylpalladium chloride⁷ and the cyclobutenyl complexes $[\text{Ph}_4\text{C}_4\text{OC}_2\text{H}_5]_2\text{Pd}_2\text{Cl}_2$ ⁸ all form crystals in which the molecules have crystallographic centres of symmetry at the mid-points of the halogen bridges (molecular symmetry C_2); in these cases the palladium atoms are therefore coplanar with the halogen atoms and the allyl groups are "anti". No dimeric π -allyl complex has been reported with a planar bridge but without a crystallographic centre of symmetry at the mid-point of that bridge.

Intermolecular contacts less than 4.0 Å were calculated for compound (I); there are no specific interactions that would obviously account for the nonplanarity of the palladium–bromine bridge. The intramolecular Pd–Pd distance, 3.32 Å, is similar to the interionic Pd–Pd distances 3.25–3.35 Å in $\text{Pd}(\text{NH}_3)_4$, $\text{Pd}(\text{halogen})_4$.⁹ Direct metal–metal bonding, such as is found in the nonplanar chloro-bridged complexes $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ¹⁰ and $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ ¹¹ and also in $[\text{Pd}(\text{allyl})\text{acetate}]_2$,¹² seems unlikely in compound (I) which is diamagnetic.

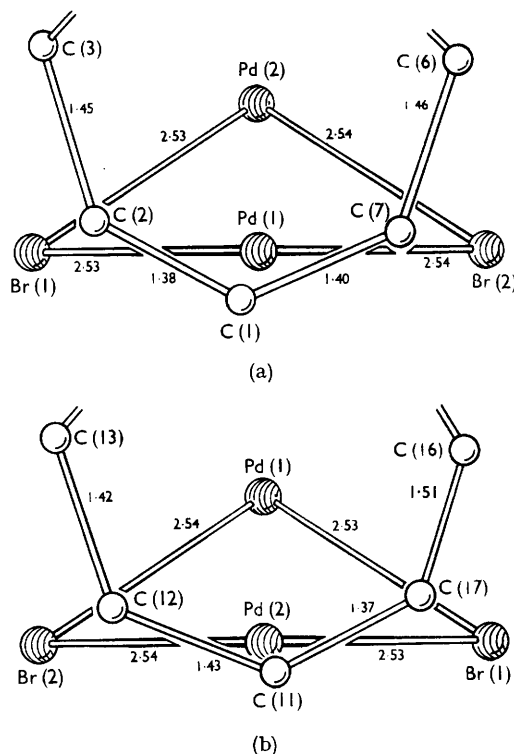


FIGURE 2 (a) and (b). Positions of the allylic carbon atoms relative to the bromine–palladium–bromine planes; the direction of view is along the external bisector of the angle Br–Pd–Br.

The arrangements of the allyl groups are not exactly symmetrical with respect to the Br–Pd–Br planes (see Figure 2) and the two arrangements themselves differ from each other. The perpendicular displacements of the allylic carbon atoms are C(1) -0.38 Å, C(2) $+0.25$ Å, and C(7) $+0.14$ Å with respect to the Br(1)–Pd(1)–Br(2) plane, and C(11) -0.24 Å, C(12) $+0.28$ Å and C(17) $+0.36$ Å with respect to the Br(1)–Pd(2)–Br(2) plane. (The estimated standard deviations

of the positions of the allylic carbons are about 0.02 Å.) This lack of symmetry in the binding of the two allyl groups and the nonplanarity of the bridge support the suggestion² that the inherent lack of rigidity in molecules of the present type allows "crystal-packing" forces to determine the conformation adopted in the solid state.

The plane containing the allyl group C(2)-C(1)-C(7) makes a dihedral angle of 118° with the palladium-bromine co-ordination plane and of 143° with the plane defined by the four effectively coplanar atoms C(2), C(3), C(7), and C(6). For the other cycloheptenyl ring the corresponding values, 124° and 143° respectively, are very similar.

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