Bis-π-allylrhodium Chloride

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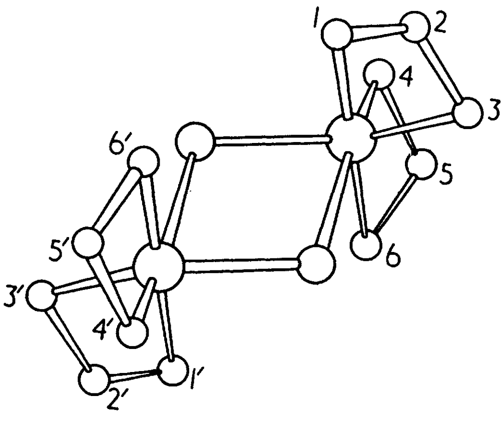
STRUCTURAL analyses of several allyl complexes of nickel[1] and palladium[2–4] have shown interesting features of the metal–allyl bond.[5] In the case of triphenylphosphinemethallylpalladium chloride[6] the X-ray analysis[4] confirmed the suggestions made from studies of the proton magnetic resonance spectrum; the methallyl group was asymmetrically bonded to the palladium ion in the sense that, in contrast to the situation in π-allylpalladium chloride, the metal–carbon bond lengths are nonequivalent. Nuclear magnetic resonance data on bis-π-allylrhodium chloride[7] and tris-π-allylrhodium[8] have also been interpreted in terms of asymmetric metal–allyl bonding.

A single-crystal analysis has now been completed ($R = 0{\cdot}088$ for 1409 independent reflexions) for the bis-π-allylrhodium chloride dimer, the molecular stereochemistry of which is shown in the Figure. Each rhodium(I) ion can be thought of as having approximately octahedral co-ordination symmetry. The molecule has exact C_{i} symmetry in the crystal and several features of the molecular geometry are of importance.

(i) The two crystallographically nonequivalent rhodium–chlorine bonds have lengths of 2·511 and 2·469 Å respectively. Each of these bond lengths has a standard deviation of 0·004 Å so that the difference of 0·042 Å is highly significant. We have, at present, no convincing explanation for this difference; it is very similar to that reported for the Rh–Cl bonds in the rhodium dicarbonyl chloride dimer[9] where again it is difficult to see a reason for such a distortion. The mean Rh–Cl bond length in the bisallyl complex is 2·49 Å, 0·14 Å greater than that in $Rh(CO)_2Cl$.

(ii) The metal–carbon and carbon–carbon bond lengths in the bisallyl complex are shown in Figure 2a, and, for comparison, the related results[4] for the triphenylphosphinemethallylpalladium chloride are shown in Figure 2b. The agreement between chemically equivalent bonds for the two crystallographically nonequivalent metal–allyl interactions in $[(\pi\text{-}C_3H_5)_2RhCl]_2$ is good, the mean metal–carbon and carbon–carbon standard deviations being 0·02 and 0·03 Å respectively; the correlation with the Pd–C and C–C bond lengths in $Ph_3P{\cdot}PdCl\text{–}\pi\text{-}C_3H_4{\cdot}CH_3$ is also good. As such, the structural basis for asymmetrically bonded π-allyl groups is beginning to become clear. The two shortest Rh–C bonds in $[(\pi\text{-}C_3H_5)_2RhCl]_2$ are effectively *trans* to the two bridging chlorine



FIGURE

atoms while the shortest Pd–C bond in $Ph_3P\cdot PdCl$–π-C_3H_5 is again *trans* to the chlorine. In an extreme representation of the bonding in these molecules, the structure could be written as (I), although such a formula is open to misunderstanding.

It would be of obvious interest to know the conformation of the two methylene groups with respect to the plane containing the allyl carbon atoms. In both (π-$C_3H_4\cdot CH_3)_2Ni$ and $Ph_3P\cdot PdCl$–π-$C_3H_4\cdot CH_3$ the 2-substituted methyl-carbons deviate significantly from the plane of the allyl group. The bond-length data presently available suggests that the metal–carbon bond, written formally as a σ-bond in (I) contains more *p*-orbital character than results from the interaction of the metal with symmetrical allyl molecular orbitals. Equally, the terminal carbon–carbon bond b–c has a lower π-bond order than in the free ligand. This situation could be achieved by a rotation of the terminal methylene group; the barrier to rotation of terminal methylene groups in tris-π-allyl rhodium has been estimated[8] as *ca.* 10 kcal./mole.

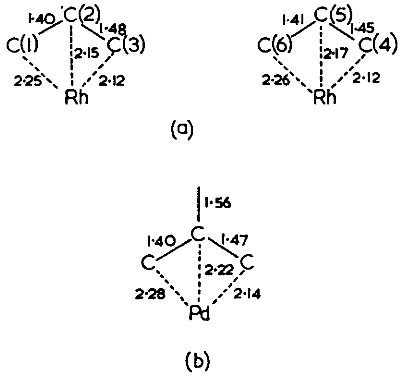
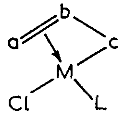


FIGURE 2



(I)

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[1] H. Dietrich and R. Uttech, *Naturwiss.*, 1963, **50**, 613.
[2] A. E. Smith, *Acta Cryst.*, 1965, **18**, 331.
[3] M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777.
[4] R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.
[5] S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, 1966, **5**, 573.
[6] J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 79.
[7] J. Powell and B. L. Shaw, *Chem. Comm.*, 1966, 236.
[8] J. K. Becconsall and S. O'Brien, *Chem. Comm.*, 1966, 720.
[9] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.