The Molecular Structure of an Allene Complex with Rhodium(I)

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RECENTLY allenes have been used as co-ordinating ligands in transition-metal ion complexes,[1,2] though the type of bonding involved is not yet known. We present the preliminary results of a crystal structure analysis of acetylacetonatebis(tetramethylallene)rhodium(I).† The two tetramethylallene ligands function formally as π-bonded mono-olefins, the central C=C=C system of each being approximately at 90° to the co-ordinating plane. Furthermore in both ligands the three central carbon atoms are not linear and the two C=C bonds differ in length.

$(C_5H_7O_2)Rh(C_7H_{12})_2$ recrystallizes as reddish-brown needles in the monoclinic space group $P2_1/n(C^5_{2h})$[3] with a = 13·075 ± 1, b = 18·980 ± 3, c = 8·2264 ± 5 Å, β = 96·35° ± 5°, U = 2028·9 Å^3, D_m = 1·294 for Z = 4, M = 395·4. Complete three-dimensional data to sin θ = 0·42 (Mo-K_α radiation) were collected on the Nonius three-circle automatic single-crystal diffractometer with the θ—2θ scan method. The structure was determined by conventional Patterson, Fourier, and least-squares refinement methods, R = 0·050 (not including hydrogen atoms) for 2389 independent reflections.

The molecular structure together with important bond lengths and angles is shown in the Figure. The rhodium ion is in approximately square-planar co-ordination [deviations of centres of bonds C(8)–C(9) and C(1)–C(2) from Rh, O(1), O(2) plane being 0·36 Å and −0·29 Å, respectively], acetylacetonate being bidentate, O(1)–Rh–O(2) = 87·4°, and each tetramethylallene molecule acting as a monodentate ligand, O(1)–Rh–[C(9) : C(8)] = 87·9°, [C(9) : C(8)]–Rh–[C(2) : C(1)] = 98·3°. The dihedral angles between the O(1)–Rh–O(2) plane and the planes through C(9)–C(8)–C(10) and C(2)–C(1)–C(3) are 99·8° and 101·4°, respectively. The C(2)–C(1) and C(9)–C(8) bonds are inclined at angles of 96·3° and 96·7°, respectively, to the O(1)–Rh–O(2) plane. The distances of the rhodium ion to the centres of the C(9)–C(8) and C(2)–C(1) bonds are both 1·99 Å, comparing

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† Prepared by H. C. Volger, K. Vrieze, and Miss M. Gronert from $(C_5H_7O_2)Rh(C_2H_4)_2$ and tetramethylallene in methanol, personal communication.

well with that found for other olefinic-type ligands, *e.g.* $RhCl(C_8H_{12})$ dimer,[4] where the corresponding distance equals 2·00 Å. The Rh–O bonds [Rh–O(1) = 2·08 Å, Rh–O(2) = 2·07 Å] are normal in length[5] and the six-membered ring formed by Rh, O(1), C(16), C(15), C(17), and O(2) is planar (maximum deviation from plane = 0·04 Å). The C(16)–O(1), C(17)–O(2), C(15)–C(16), and C(15)–C(17) bonds are intermediate in length between single and double bonds and further confirm that the chelate ring exhibits the enolate-type resonance found in other acetylacetonate complexes.[6]

If the molecular geometry of the co-ordinated allene ligands is compared with that in the free ligand, two important changes are seen: (i) the central C=C=C system is no longer linear, the non-bonded carbon atoms C(3) and C(10) being bent away from the rhodium ion, C(3)–C(1)–C(2) = 148·9° and C(9)–C(8)–C(10) = 147·2 and (ii) there is a significant difference in the central C=C bond-lengths, the longer bond being formally co-ordinated (C=C in allene = 1·309 Å).[7]

The dihedral angles between planes C(12), C(9), C(11) and C(13), C(10), C(14) and between planes C(4), C(2), C(5) and C(6), C(3), C(7) are 90·9° and 91·6°, respectively, thus remaining close to the free-ligand value of 90°.

The usual description of bonding in π complexes of unsaturated organic ligands with transition metals[8] implies both loss of bonding electron density in the co-ordinating bond(s) and activation of the co-ordinating ligand.[9] The presence of the rhodium ion changes the energy of the ligand molecular-orbitals in such a way as to facilitate transfer of electron density to the lowest antibonding molecular orbital. It is well known that molecules such as CO_2, $H_2C{\cdot}CO$, and $H_2C{:}C{:}CH_2$ are not linear in the first excited-state.[10] Unfortunately the structural parameters of tetramethylallene in the first excited-state are not known and such firm conclusions as were possible with the complex $Pt(CS_2)(PPh_3)_2$[11] cannot be drawn. Tetramethylallene and carbon disulphide are, however, comparable systems in this context and it is not unreasonable to describe the geometry of the allene ligand in the complex as resembling that of the first excited state of the free ligand.

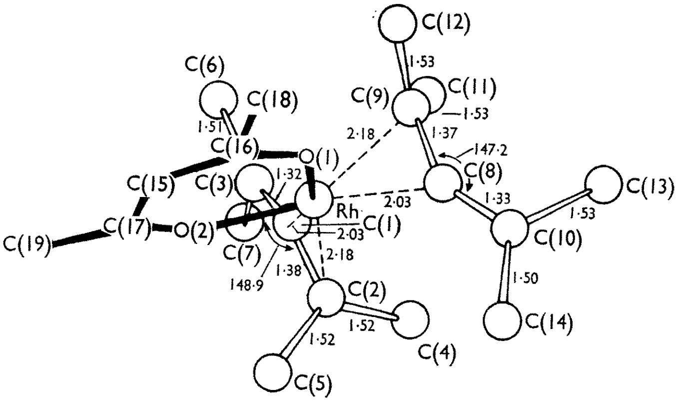

FIGURE. *The molecular structure of* $(C_5H_7O_2)Rh(C_7H_{21})_2$ (bond lengths in Å). *Estimated standard deviations are* ±0·02 Å *for* Rh-C *and* ±0·03 Å *for* C–C.

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