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The Structure of the Allene–Metal Complex, Iodobis(triphenylphosphine)allenerhodium

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The rhodium–allene complex, $RhX(PPh_3)_2C_3H_4$ (X = Cl, Br, or I), catalyses the tetramerization and polymerization of allene [1] but the platinum–allene comples, $Pt(PPh_3)_2C_3H_4$, does not [2] We have now made X-ray analyses of both the rhodium- and platinum–allene complexes, and report the structure of the rhodium–allene complex.

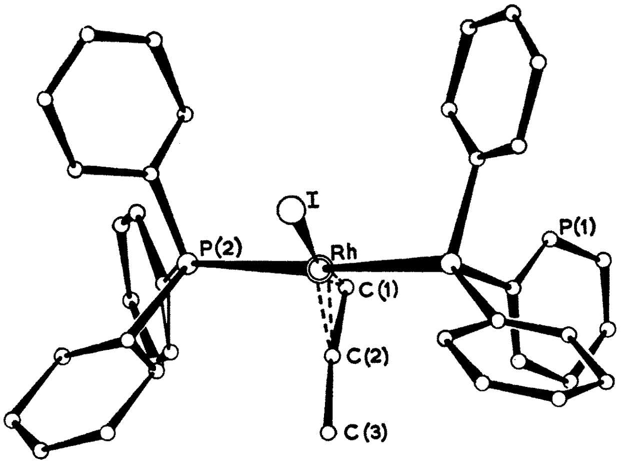

FIGURE 1. *Structure of* $RhI(PPh_3)_2C_3H_4$, *viewed along the* b *axis.*

Iodobis(triphenylphosphine)allenerhodium, $RhI(PPh_3)_2C_3H_4$, crystallizes as deep orange orthorhombic crystals. Crystal data: $a = 22{\cdot}07_7$, $b = 18{\cdot}78_2$, and $c = 16{\cdot}85_5$ Å, $Z = 8$, $D_c = 1{\cdot}50_9$ g.cm.$^{-3}$, space group *Pbca*. The intensities of 3273 reflexions were measured on a General Electric XRD-5 diffractometer equipped with a single-crystal orienter using Mo-K_α radiation. The structure was solved by usual Patterson and Fourier methods, and refined by a block-diagonal least-squares procedure. Anisotropic thermal parameters were used only for the rhodium, iodine, and phosphorus atoms. More cycles of refinement were carried out but the discrepancy factor R did not decrease as much as expected, the value being 0·179 for 2493 non-zero reflexions. The structure obtained, however, is considered to be correct since the interatomic distances and angles are reasonable within experimental error.

The geometry of the rhodium atom co-ordination is shown in Figure 2, together with bond distances and angles and their estimated standard deviations, which are large because of the high R value. The rhodium atom and its neighbouring atoms, I, P(1), and P(2), lie approximately on the same plane and the C(1)–C(2) bond makes an angle of 76° with this plane. The rhodium atom has square-planar co-ordination, if the allene ligand is considered as monodentate. The C(1)–C(2) bond intersects the basal plane of the rhodium atom one-fourth (0·35 Å) of the way along the C(1)–C(2) distance as is found in $[PdCl_2(CH_2{\cdot}CHPh)]_2$.[3] The Rh–C(1) distance is slightly longer than Rh–C(2), but the difference is not significant. The Rh–C(3) distance is much greater (3·02 Å). The allene ligand co-ordinates to the rhodium atom by only one of the two adjacent double bonds, and the ligand is not linear, [angle C(1)–C(2)–C(3) 158°]. Co-ordination similar to this is also found in $Pd(PPh_3)_2CS_2$[4] and $Pt(PPh_3)_2CS_2$.[5] The

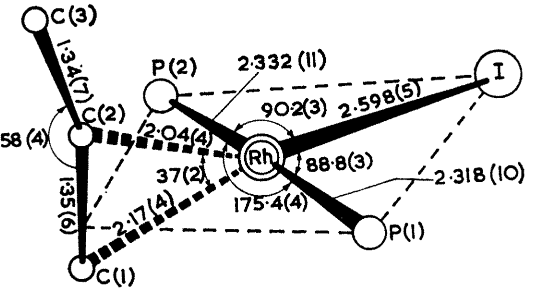

FIGURE 2. *Geometry of the rhodium atom co-ordination.* (*Estimated standard deviations in parentheses.*)

Rh–I, Rh–P, and other distances are comparable to the previously determined values. The two triphenylphosphine groups are staggered by *ca.* 13° from the eclipsed position.

Crystal data for the bromo-complex, $RhBr(PPh_3)_2C_3H_4$, are $a = 22{\cdot}09_9$, $b = 18{\cdot}66_4$, $c = 16{\cdot}83_8$ Å, $Z = 8$; space group *Pbca*. The bromo-complex is considered to be isostructural with the iodo-complex.

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