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Preliminary communication

Localized bonding in a π-cyclopentadienyl ring: The crystal structures of two π-diene-π-cyclopentadienylrhodium(I) complexes

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Rhodium(I) complexes of monoolefins and non-conjugated diolefins are well known but few complexes with conjugated diolefins have been reported[1] and only in one case has a structural analysis been carried out. This is chlorodibutadienerhodium in which the two molecules are coordinated in a bidentate manner, the chlorine atom occupying the apical position of an approximate square pyramid[2]. We have prepared a large number of rhodium(I) complexes of conjugated diolefins which exemplify both bidentate and monodentate coordination of the diolefin, the preparation and properties of which will be described separately. We here report the results of an X-ray investigation of two of these complexes, π-2,3-dichlorobutadiene-π-cyclopentadienylrhodium(I) (I) and π-2,3-dimethylbutadiene-π-cyclopentadienylrhodium(I) (II). An analogous complex is also formed by butadiene itself but neither of the substituted butadienes forms a bisdiolefin rhodium(I) chloride.

The two complexes were prepared from tetrakis(ethylene)dirhodium(I) dichloride by displacement of ethylene by diolefin and subsequent reaction with thallium cyclopentadienide. They were characterised by ^{1}H NMR, IR and mass spectra and by elemental analysis. [(I) Found: C, 37.3; H, 3.3; Cl, 24.5%. $C_9H_9Cl_2Rh$ calcd.: C, 37.1; H, 3.1; Cl, 24.4%. (II) Found: C, 52.6; H, 6.0%. $C_{11}H_{15}Rh$ calcd.: C, 52.8; H, 6.0%].

Orange needles of I and II are isomorphous, monoclinic, spacegroup $P2_1/n$, $Z = 4$. For I, $C_9H_9Cl_2Rh$, $M = 289.9$, $a = 14.796(15)$, $b = 5.718(7)$, $c = 12.490(14)$ Å, $\beta = 112.82(12)°$, $U = 972.3$ Å^3, $d_m = 2.00$ (2), $d_c = 1.98$. For II, $C_{11}H_{15}Rh$, $M = 250.1$, $a = 14.844(12)$, $(b) = 5.852(7)$, $c = 12.676(14)$ Å, $\beta = 113.95(13)°$, $U = 1002.7$ Å^3, $d_m = 1.68(2)$, $d_c = 1.66$. The intensities of 1724 (I) and 1752 (II) independent reflections ($2\theta < 50°$) were recorded using Zr-filtered Mo-$K\alpha$ radiation on a GE XRD 5 manual diffractometer by the stationary-crystal—stationary-counter method.

The structures were solved from Patterson and Fourier syntheses. Least-squares refinements using, for compound I, 1177 reflections with $I > \sigma(I)$ and, for compound (II), 1199 reflections with $I > 2\sigma(I)$ have given respective R values of 0.057 and 0.055. Rh, Cl and C atoms were refined anisotropically while parameters for the non-methyl hydrogen atoms were estimated and included in the structure factor calculation but not refined. The molecules (Fig.1) have approximate mirror planes running through atom C(1) and the mid-points of the C(3)–C(4) and C(7)–C(8) bonds. The π-cyclopentadienyl ring and the butadiene group are both planar within experimental error in I and II. The C(1) end of the ring is tilted towards the plane of the diene, the two planes intersecting at 12.3 and 10.6° in the two structures. The metal atom is, respectively, 1.88 and 1.64 Å (I) and 1.87 and 1.67 Å (II) from these two least-squares planes.

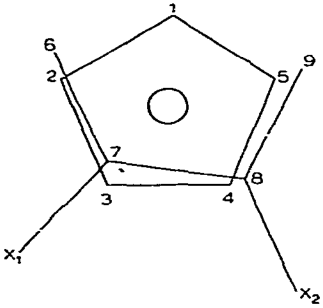

Fig. 1. Projection of complex II onto the cyclopentadiene ring. Although pertaining specifically to II the Figure is adequate to describe I.

There are no significant variations in the carbon–carbon or, for the most part, in the rhodium–carbon distances relating to the butadiene moiety of either molecule (see Table 1) though it is interesting that in both compounds the diene lies slightly closer to the metal than in chlorodibutadienerhodium[2].

Considering the π-cyclopentadienyl moiety there is evidence both from the rhodium–carbon and the carbon–carbon distances for a small but significant measure of localised bonding in the cyclopentadienyl ring in the case of the dichloro complex (I). We note, firstly, that there are two long bonds, Rh–C(3) and Rh–C(4), and three short bonds, Rh–C(1), Rh–C(2) and Rh–C(5), the mean difference between the two sets being ca. four times the standard deviation. These inequalities are matched by corresponding inequalities in the carbon–carbon distances. Thus, atoms C(3) and C(4) that lie furthest from the metal are themselves closest together, while the carbon atoms that encompass the two longest bonds, C(2)–C(1) and C(1)–C(5), are those that lie closest to the metal. Inequalities in ring carbon–carbon distances in unsubstitited π-cyclopentadienyl compounds have been noted previously and both steric and electronic explanations have been advanced[3]. However, the observed distortions often appear random or they fail to conform satisfactorily to any particular model. In contrast, the patterns of variation in the carbon–carbon distances and in the metal–carbon distances in I reinforce each other

TABLE 1

BOND LENGTHS (Å) FOR COMPLEXES I AND II

	I *(X = Cl)*	*II* *(X = CH_3)*
C(1)–C(2)	1.450(26)	1.438(22)
C(2)–C(3)	1.323(24)	1.397(20)
C(3)–C(4)	1.310(27)	1.357(26)
C(4)–C(5)	1.375(27)	1.369(26)
C(5)–C(1)	1.410(26)	1.381(21)
C(6)–C(7)	1.43(2)	1.45(2)
C(7)–C(8)	1.44(2)	1.45(2)
C(8)–C(9)	1.41(2)	1.42(2)
C(7)–X(1)	1.73(1)	1.52(2)
C(8)–X(2)	1.73(1)	1.51(2)
Rh–C(1)	2.187(19)	2.175(18)
Rh–C(2)	2.188(16)	2.210(14)
Rh–C(3)	2.258(17)	2.238(19)
Rh–C(4)	2.248(15)	2.226(19)
Rh–C(5)	2.187(14)	2.205(21)
Rh–C(6)	2.123(15)	2.170(14)
Rh–C(7)	2.097(14)	2.110(13)
Rh–C(8)	2.086(10)	2.102(16)
Rh–C(9)	2.137(12)	2.136(11)

in a consistent manner and seem unlikely to the due merely to crystal packing effects. There seems no reason to expect a specifically π-allyl type of localisation in this compound as has sometimes been suggested[4]. If this occurred then C(2)–C(3) and C(5)–C(4) should be the longest bonds which is not observed. Rather, it seems more reasonable to assume as argued by Cotton[5], a gradation in carbon–carbon bond order which varies (inversely) in sympathy with metal–carbon bond order. Carbon–carbon and rhodium–carbon bond length differences in compound (II) are not in themselves significant though it is notable that the pattern of variation is precisely that found for I.

The occurrence of measurable distortion in I but not in II may find an explanation in the different bonding characteristics of the two dienes. As pointed out by Mason and co-workers[4,6] the metal d_{xz} and d_{yz} orbitals (and the cyclopentadienyl e_1^+ and e_1^- orbitals with which they overlap) are not expected to remain degenerate in complexes lacking cylindrical symmetry. Both chemical and NMR evidence[7] suggests, in accord with electronegativity considerations, that I is a better acceptor of d_π electrons than II. This should further lift the degeneracy of d_{xz} and d_{yz} (for example, through an improved overlap of d_{yz} with ψ_3, the first anti-bonding π-orbital of the diene) and thus to promote, preferentially, electron donation from those carbon atoms, C(1), C(2) and C(5), *trans* to the diene. No inequivalence in the ring protons was observed in the ^{1}H NMR spectrum of an acetone solution of I down to −60°

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