Journal of Organometallic Chemistry, 265 (1984) 305–310
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

X-RAY CRYSTAL STRUCTURE OF (η^5-PENTAMETHYLCYCLOPENTADIENYL)(η^3-1,3-DIMETHYLALLYL)CHLORORHODIUM: LOCALIZED "DI-π-OLEFIN-σ" BONDING OF CYCLOPENTADIENYL

A.S. BATSANOV and Yu.T. STRUCHKOV*

Nesmeyanov Institute of Organoelement Compounds of the U.S.S.R. Academy of Sciences, 28 Vavilov Str., Moscow (U.S.S.R.)

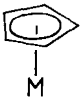
(Received November 22nd, 1983)

Summary

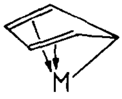
The crystal structure of (η^5-C_5Me_5)(η^3-MeHC$\cdots$CH$\cdots$CHMe)RhCl at −120°C was determined ($R = 0.041$ for 1790 reflections). The molecule has approximate mirror symmetry. The cyclopentadienyl ring is bent by 6.8°, acquiring an envelope-like conformation, and its bonding with Rh is of a partially-localized $\eta^4:\eta^1$ type with Rh–C("π-diolefin") of 2.206–2.235 Å and Rh–C("σ-bonded") of 2.151 Å. The *syn*-arrangement of the Me groups in the π-allyl ligand, assigned by NMR spectra, is confirmed.

Introduction

The possibility of localized bonding between a transition metal atom and a cyclopentadienyl ligand (i.e. deviation from the five-fold symmetry of form A) has been controversial for some time [1,2]. The most conclusive evidence of such a delocalization was later obtained from the structures of several rhodium complexes. In (η^5-C_5Ph_4Cl)Rh($CH_2{=}CH_2$)$_2$ (I) [3] and (η^5-C_5Cl_5)Rh(1,5-cyclooctadiene) (II) [4], as well as in the binuclear complexes (η^5-C_5H_5)(OC)Mn(μ-CO)$_2$Rh(CO)(η^5-C_5Me_5) (III) [5] and (η^6-C_6H_6)(CO)Cr(μ-CO)$_2$Rh(η^5-C_5Me_5)(CO) (IV) [6], the Rh–cyclopentadienyl bonding geometry is consistent with a significant contribution of form B. In the structure of (η^5-C_5Me_5)Rh(PPh_3)(C_2H_4) (V), form C is predominant [7].



(A)



(B)

(C)

In the present paper we discuss the crystal and molecular structure of yet another complex of this class, viz. (η^5-C_5Me_5)(η^3-MeHC$\cdots$CH$\cdots$CHMe)RhCl (VI), whose preparation and properties have been reported by Lee and Maitlis [8].

0022-328X/84/$03.00

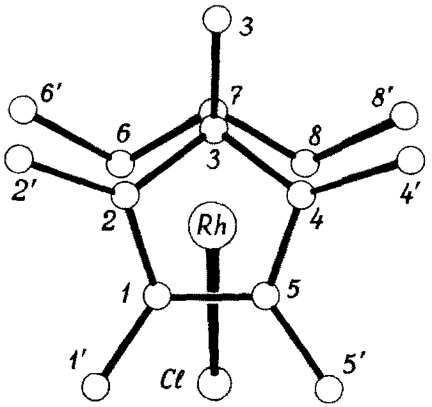


Fig. 1. Molecular structure of VI (projection on the mean plane of the Cp-cycle; the hydrogen atoms have been omitted).

Results and discussion

The molecular structure of VI is shown in Fig. 1; relevant bond distances and angles are listed in Table 1. The molecule has a non-crystallographic mirror symmetry plane through Rh, Cl, C(3), C(3′) and C(7), and the midpoint of the C(1)–C(5) bond.

The geometry of the cyclopentadienyl ring in VI is similar to that in complexes I–IV. The C(1), C(2), C(4) and C(5) atoms are coplanar within 0.01 Å (less than 1.5σ), while C(3) is bent by 0.10 Å out of their mean plane towards the Rh atom. Thus the cycle adopts an envelope conformation, being folded along the line

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°)

Bond		Bond		Bond	
Rh–Cl	2.418(2)	Rh–C(7)	2.117(8)	C(2)–C(2′)	1.52(1)
Rh–C(1)	2.217(7)	Rh–C(8)	2.191(8)	C(3)–C(3′)	1.50(1)
Rh–C(2)	2.235(7)	C(1)–C(2)	1.41(1)	C(4)–C(4′)	1.52(1)
Rh–C(3)	2.151(7)	C(2)–C(3)	1.45(1)	C(5)–C(5′)	1.51(1)
Rh–C(4)	2.215(7)	C(3)–C(4)	1.45(1)	C(6)–C(7)	1.43(1)
Rh–C(5)	2.206(7)	C(4)–C(5)	1.423(11)	C(7)–C(8)	1.39(1)
Rh–Cp[a]	1.838	C(5)–C(1)	1.435(11)	C(6)–C(6′)	1.50(1)
Rh–C(6)	2.199(7)	C(1)–C(1′)	1.48(1)	C(8)–C(8′)	1.50(1)
Angle		**Angle**		**Angle**	
ClRhCp[a]	121.4	C(2)C(3)C(4)	106.7(6)	C(1)C(5)C(4)	109.5(7)
C(2)C(1)C(5)	107.1(6)	C(2)C(3)C(3′)	127.4(7)	C(1)C(5)C(5′)	123.3(7)
C(2)C(1)C(1′)	128.4(7)	C(4)C(3)C(3′)	124.8(7)	C(4)C(5)C(5′)	126.9(7)
C(5)C(1)C(1′)	124.5(7)	C(3)C(4)C(5)	107.2(6)	C(7)C(6)C(6′)	121.4(7)
C(1)C(2)C(3)	109.0(6)	C(3)C(4)C(4′)	125.7(7)	C(6)C(7)C(8)	121.1(7)
C(1)C(2)C(2′)	125.5(7)	C(5)C(4)C(4′)	127.1(7)	C(7)C(8)C(8′)	122.5(7)
C(3)C(2)C(2′)	125.5(6)				

[a] Cp is centroid of the cyclopentadienyl ring.

C(2) · · · C(4) by 6.8° (vs. 4.2 in I and 4.6° in II). The Rh–C(3) distance of 2.151(7) Å is significantly shorter than the other Rh–C(C_5Me_5) distances (2.206–2.235, average 2.22(1) Å). The cycle involves two shorter bonds, C(1)–C(2) and C(4)–C(5), one intermediate, C(1)–C(5), and two longer bonds, C(2)–C(3) and C(3)–C(4), although the differences in their lengths are within the accuracy limits. All these features are consistent with bonding model B, the C(1), C(2), C(4) and C(5) atoms forming a π-coordinated pseudo-diolefin moiety and the C(3) atom being σ-bonded to rhodium.

Day et al. [4] assumed that the following features (common for complexes I and II) could favour the confirmation of structure B: (1) a local or crystallographic mirror symmetry of the Rh atom coordination environment, eliminating the degeneration of metal–cyclopentadienyl bonding orbitals (a pseudo-σ-bonded carbon atom of the cycle is situated in the mirror plane); (2) bulky substituents at all five atoms of the Cp ring; (3) a halogen substituent at the pseudo-σ-bonded carbon. The structures of III, IV and VI demonstrate that the third condition, as well as non-identity of the substituents in the Cp ring (existing in I), is not indispensable. On the contrary, the first two conditions are fulfilled not only by all the complexes (I–IV and VI) with bonding model B, but also by V.

On the other hand, localization of metal–cyclopentadienyl bonding in VI can be induced by the *trans*-influence of other ligands. The pseudo-diolefin system in the cycle is in an approximate *trans*-position to the π-allyl ligand, while the pseudo-σ-bonded C(3) atom is almost *trans* to the chlorine atom (the ClRhC(3) angle is 156.2(2)°), which is an extremely poor electron donor. It is noteworthy that in C_5Me_5 complexes of rhodium, even in the case of delocalized (type A) bonding, the Rh–C(C_5Me_5) distances are significantly different and very sensitive to the nature of *trans* ligands [9].

In C_5Me_5 complexes, the methyl carbons are always inclined out of the ring plane, away from the metal atom [9]. The same effect is observed in VI, where the C(1)–C(1′), C(2)–C(2′), C(4)–C(4′) and C(5)–C(5′) bonds are bent out of the "π-diolefin" moiety C(2)C(1)C(5)C(4) plane by 1.9, 4.3, 4.1 and 5.3°, respectively. The angle between the C(3)–C(3′) bond and the C(2)C(3)C(4) plane is larger (9.5°), in agreement with the stronger sp^3-character of C(3).

The π-allyl ligand is symmetrically coordinated to the rhodium atom. The terminal atoms C(6) and C(8) of this ligand are equidistant from Rh, and the central atom C(7) is closer to it by 0.08 Å. Such a coordination of the π-allyl ligand is typical for transition metal complexes in general [10] but less common for rhodium complexes. Thus, in the complexes $[(\pi\text{-allyl})_2RhX]_2$ (X = Cl [11] and Br [12]), the π-allyl coordination is strongly unsymmetric (probably due to the *trans*-influence). In (2-methylallyl)Rh$(AsPh_3)_2Cl_2$, the central atom of the allyl moiety is further from the metal (Rh–C 2.267 Å) than the terminal atoms (2.246 and 2.226 Å) [13].

In molecule VI, the π-allylic moiety is tilted by its central atom C(7) towards the C_5Me_5 ligand, and forms a dihedral angle of 13.7° with the mean plane of the latter. A similar non-parallel arrangement of the π-allyl and π-cyclopentadienyl ligands (dihedral angle 19.5°) was found in CpPd(π-C_3H_5), but in this case, the allyl group is bent towards the planar Cp-ligand by its terminal carbon atoms [14].

Both methyl substituents in the allyl ligand are in *syn*-positions relative to the central hydrogen atom H[C(7)], in agreement with the assignment of Lee and Maitlis [8] based on the ^1H NMR spin–spin coupling constant (J 10 Hz). Both methyl

TABLE 2

PLANES IN THE STRUCTURE OF VI [a]

Equation of the planes $Ax + By + Cz - D = 0$

Plane	A	B	C	D
I	0.9518	−0.2816	−0.1217	1.6162
II	0.9361	−0.1487	−0.3187	−2.4864
III	0.9538	−0.2610	−0.1491	1.5700
IV	0.9437	−0.3270	−0.0502	1.8522

Deviations of atoms from the plane (σ = 0.007–0.009, for Rh 0.001 Å) (Å)

Plane	Atoms defining the plane	Other atoms
I	C(1) −0.02, C(2) −0.04, C(3) −0.04, C(4) 0.03, C(5) 0.00	Rh −1.837, C(6) −3.45, C(7) −3.26, C(8) −3.40, C(6′) −3.21, C(8′) −3.14
II	C(6), C(7), C(8)	Rh 1.753, C(6′) 0.09, C(8′) 0.07
III	C(1) −0.01, C(2) 0.01, C(4) −0.01, C(5) 0.01	Rh −1.858, C(3) −0.10, C(1′) 0.04, C(2′) 0.12, C(3′) −0.03, C(4′) 0.10, C(5′) 0.15.
IV	C(2), C(3), C(4)	C(3′) 0.25

[a] Angle between planes I and II = 13.7°; between III and IV = 6.8°.

carbons are tilted out of the π-allyl moiety plane towards the rhodium atom (see Table 2).

The Rh–Cl bond length in VI (2.418(2) Å) is slightly longer than the terminal Rh–Cl bond lengths in $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$ (2.393 Å) [15] and $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$ (2.397 Å) [16], probably due to the stronger σ-character of the *trans* Rh–C(3) bond.

Experimental

X-Ray experiments were performed with a Syntex $P2_1$ four-circle computer-controlled diffractometer, using graphite-monochromated Mo-K_α radiation. Calculations were performed with an Eclipse S/200 computer using INEXTL programs [17].

Crystal data of VI: $C_{15}H_{24}ClRh$, monoclinic, at −120°C a 7.454(3), b 14.655(6), c 13.791(5) Å, β 95.21(3)°, V 1500 Å^3, $Z = 4$, $d_{\text{calc.}}$ 1.52 g cm^{-3}, space group $P2_1/c$.

Cell constants and intensities of 1790 independent reflections with $I \geqslant 2\sigma(\theta/2\theta$ scan, $\theta \leqslant 26°$) were measured at −120°C. The Rh atom was located in a Patterson function, and other non-hydrogen atoms in subsequent Fourier electron-density maps. These atoms were refined by a full matrix least-squares technique using isotropic temperature factors to $R = 0.063$, and using anisotropic factors to $R = 0.053$ (with anomalous dispersion corrections for Rh and Cl). All the hydrogen atoms were located from difference Fourier synthesis and were included as fixed contributions (with assumed B_{iso} 5.0 Å^2) in the further refinement, which gave $R = 0.041$ and

TABLE 3

ATOMIC COORDINATES ($\times 10^4$; for Rh $\times 10^5$) AND ANISOTROPIC THERMAL FACTORS $T = \exp[-0.025(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	10028(7)	6415(4)	23312(4)	14.4(2)	9.0(2)	15.6(2)	0.8(2)	0.9(2)	1.2(3)
Cl	−634(2)	1736(1)	1278(1)	19.2(7)	14.5(7)	21.5(8)	3.3(6)	−0.2(6)	4.3(7)
C(1)	2936(9)	318(5)	1250(6)	13(3)	17(3)	22(3)	4(3)	−1(3)	3(3)
C(2)	2818(9)	−452(5)	1853(5)	17(3)	9(3)	22(3)	5(2)	1(3)	−4(3)
C(3)	3269(10)	−184(5)	2861(5)	17(3)	12(3)	18(3)	6(3)	−4(3)	3(3)
C(4)	3899(10)	748(5)	2843(5)	17(3)	20(3)	24(4)	3(3)	3(3)	−4(3)
C(5)	3636(10)	1053(5)	1860(6)	16(3)	10(3)	29(4)	5(3)	4(3)	2(3)
C(1′)	2551(10)	381(6)	178(6)	25(4)	27(4)	17(3)	4(3)	4(3)	0(3)
C(2′)	2305(12)	−1408(5)	1505(6)	33(4)	15(4)	29(4)	6(3)	0(3)	−2(3)
C(3′)	3441(11)	−791(6)	3738(6)	31(3)	25(4)	29(4)	11(3)	−3(3)	6(3)
C(4′)	4737(11)	1282(6)	3716(6)	23(4)	26(4)	30(4)	−1(3)	−4(3)	−10(3)
C(5′)	4148(10)	1968(6)	1472(6)	20(3)	19(4)	37(4)	−2(3)	7(3)	3(3)
C(6)	−1594(10)	−29(5)	2488(6)	15(3)	22(4)	25(4)	−3(3)	5(3)	4(3)
C(7)	−769(10)	306(5)	3393(6)	19(3)	19(3)	18(3)	2(3)	7(3)	2(3)
C(8)	−379(10)	1226(5)	3523(6)	20(3)	17(4)	27(4)	4(3)	10(3)	6(3)
C(6′)	−1910(11)	−1032(6)	2319(7)	27(4)	15(3)	38(5)	−6(3)	3(3)	9(3)
C(8′)	571(11)	1594(6)	4445(6)	34(4)	22(4)	22(4)	−2(3)	6(3)	−3(3)

TABLE 4

COORDINATES ($\times 10^3$) OF THE HYDROGEN ATOMS

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H[C(1′)]	371	38	−16	H[C(5′)]	536	190	112
H′[C(1′)]	164	84	−19	H′[C(5′)]	411	231	198
H″[C(1′)]	224	−20	−15	H″[C(5′)]	281	223	117
H[C(2′)]	175	−170	201	H[C(6)]	−251	49	209
H′[(2′)]	160	−130	84	H[C(6′)]	−152	−118	158
H″[(2′)]	351	−177	154	H′[C(6′)]	−326	−123	241
H[C(3′)]	309	−43	442	H″[C(6′)]	−122	−142	272
H′[C(3′)]	259	−124	362	H[C(7)]	−42	−26	395
H″[C(3′)]	434	−101	383	H[C(8)]	−112	162	308
H[C(4′)]	428	104	436	H[C(8′)]	150	209	426
H′[C(4′)]	621	138	371	H′[C(8′)]	−29	181	491
H″[C(4′)]	417	188	354	H″[C(8′)]	149	112	484

$R_w = 0.043$. A weighting scheme, $W = \sigma_F^{-2}$, was used (accuracy of fit 2.26). The positional and thermal atomic parameters are listed in Tables 3 and 4.

Acknowledgements

The authors are grateful to Prof. Z.A. Rubezhov and Dr. Z.L. Lutsenko for providing crystal samples for crystallographic study, and fruitful discussions.

References

1 P.J. Wheatley in J.D. Dunitz and J.A. Ibers (Eds.), Perspectives in Structural Chemistry, Wiley, New York, 1967, Vol. 1, p. 23.
2 L.J. Guggenberger and R. Cramer, J. Am. Chem. Soc., 94 (1972) 3779.
3 V.W. Day, B.R. Stults, K.J. Reimer and A. Shaver, J. Am. Chem. Soc., 96 (1974) 1227.
4 V.W. Day, K.J. Reimer and A. Shaver, J. Chem. Soc., Chem. Commun., (1975) 403.
5 M.L. Aldridge, M. Green, J.A.K. Howard, G.N. Pain, S.J. Porter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 1333.
6 R.D. Barr, M. Green, K. Marsden, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 507.
7 W. Porzio and M. Zocchi, J. Am. Chem. Soc., 100 (1978) 2048.
8 H.-B. Lee and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1975) 2316.
9 M.B. Hursthouse, K.M. Abdul Malik, D.M.P. Mingos and S.D. Willoughby, J. Organomet. Chem., 192 (1980) 235.
10 C.F. Putnik, J.J. Welter, C.D. Stucky, M.J. D'Aniello, B.A. Sosinsky, J.F. Kirner and E.L. Muetterties, J. Am. Chem. Soc., 100 (1978) 4107.
11 M. McPartlin and R. Mason, Chem. Commun., (1967) 16.
12 H. Pasternak, T. Glowiak and F. Pruchnik, Inorg. Chim. Acta, 19 (1976) 11.
13 T.G. Hewitt, J.J. de Boer and K. Anzenhoffer, Acta Crystallogr., Sect. B, 26 (1970) 1244.
14 M.Kh. Minasyants, S.P. Gubin and Yu.T. Struchkov, Zh. Strukt. Khim., 7 (1966) 906.
15 M.R. Churchill and S.W.Y. Ni, J. Am. Chem. Soc., 95 (1973) 2150.
16 M.R. Churchill, S.A. Julis and F.J. Rotella, Inorg. Chem., 16 (1977) 1137.
17 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, Kristallografiya, 28 (1983) 1029.