Unusual Bonding Patterns in Halogen-substituted η^5-Cyclopentadienyl Metal Derivatives. The Crystal and Molecular Structure of η^5-Pentachlorocyclopentadienylcyclo-octadienerhodium

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Summary Localized bonding has been observed in the η^5-C_5Cl_5 ring of the title compound which suggests appreciable contribution from a bonding model where the ring is bonded to the metal by two olefin π-bonds and one σ-alkyl bond.

Localization in the bonding of cyclopentadienyl transition-metal compounds has been an area of considerable interest and controversy for some time.[1] Usually the carbon-carbon bond distances in the cyclopentadienyl (Cp) ring are all equal (type A) but in a few cases variation in the C–C bond distances which are suggestive of a contribution from type (B) have been observed.[1a] Comparison of the bonding parameters reported for $[(\eta^1\text{-}C_5Cl_5)Mn(CO)_5]$[2] (**1**), and $[(\eta^5\text{-}C_5Ph_4Cl)Rh(C_2H_4)_2]$[3] (**2**), with those for the previously unknown title compound $[(\eta^5\text{-}C_5Cl_5)Rh(1,5\text{-}C_8H_{12})]$ (**3**)† (1,5-C_8H_{12} = cyclo-octa-1,5-diene) reveals unambiguously the appreciable contribution of the previously unreported type (C) bonding mode in the η^5-cyclopentadienyl–rhodium linkage in (**2**) and (**3**). Perspective ORTEP drawings of all three molecules are shown in the Figure.

Crystals of $[(\eta^5\text{-}C_5Cl_5)Rh(1,5\text{-}C_8H_{12})]$ (**3**), are orthorhombic, space group, P_{nma}(D_{2h}^{16}, No. 62), with a = 10·437(1), b = 12·711(1), c = 11·646(1) Å, and Z = 4. Data collection (Nb-filtered Mo-K_α radiation using θ–2θ scans on a Syntex $P\bar{1}$ Autodiffractometer) resulted in 2841 independent absorption-corrected reflections having 2θ(Mo-K_α) $<71°$ (the equivalent of 2·0 limiting Cu-K_α spheres of data) and $I > \sigma(I)$. Standard heavy-atom and difference Fourier

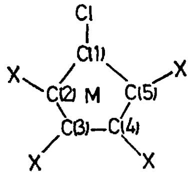

Table. Comparison of the bonding lengths (in Å) for the halogen-substituted cyclopentadienyl ligands in $[(\eta^1\text{-}C_5Cl_5)Mn(CO)_5]$ (**1**), $[(\eta^5\text{-}C_5Ph_4Cl)Rh(C_2H_4)_2]$ (**2**), and $[(\eta^5\text{-}C_5Cl_5)Rh(1,5\text{-}C_8H_{12})]$ (**3**).

Bond	(**1**)	(**2**)	(**3**)
M–C(1)	2·204(6)	2·183(4)	2·211(6)
M–C(2)	>3·00	2·299(4)	2·281(4)
M–C(3)	”	2·305(4)	2·263(4)
M–C(4)	”	2·271(4)	2·263(4)
M–C(5)	”	2·254(4)	2·281(4)
C(1)–C(2)	1·487(8)	1·451(6)	1·433(7)
C(1)–C(5)	1·499(8)	1·448(6)	1·433(7)
C(3)–C(4)	1·474(8)	1·458(6)	1·441(8)
C(2)–C(3)	1·356(8)	1·414(6)	1·399(6)
C(4)–C(5)	1·345(8)	1·418(6)	1·399(6)
C(1)–Cl	1·798(6)	1·721(5)	1·719(6)
C(2)–X	1·696(6)	1·490(6)	1·702(5)
C(3)–X	1·690(6)	1·480(6)	1·705(4)
C(4)–X	1·688(6)	1·487(6)	1·705(4)
C(5)–X	1·698(6)	1·488(6)	1·702(5)

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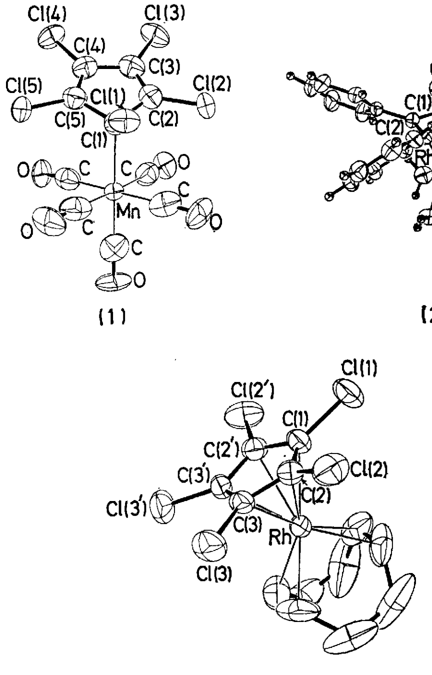
† Compounds (**1**), (**2**), and (**3**) were synthesized by insertion of the appropriate diazocyclopentadiene into the metal–chlorine bond of $[Mn(CO)_5Cl]$,[2] $[(C_2H_4)_2RhCl]_2$[3] and $[1,5\text{-}C_8H_{12})RhCl]_2$, respectively.

techniques were used to solve the structure in the noncentrosymmetric space group $Pn2_1a$. When least-squares refinement in this space group produced marked correlations between structural parameters for the two halves of the molecule which were related by a pseudo-mirror plane perpendicular to the b axis of the unit cell, the space group was changed to (the centrosymmetric) P_{nma} where the molecule can utilize a crystallographic mirror plane. Full-matrix least squares refinement using empirical weights and anisotropic thermal parameters for the eleven crystallographically independent non-hydrogen atoms has resulted in a conventional unweighted residual, R, of 0·053. The analysis shows that the crystal contains discrete $[(\eta^5\text{-}C_5Cl_5)\text{-}Rh(C_8H_{12})]$ molecules in which the Rh is η^5-bonded to the substituted cyclopentadienyl ring and π-bonded to the two double bonds of the cyclo-octadiene ligand. From the magnitudes of the anisotropic thermal parameters it is clear the molecule does not depart significantly from the C_s–m symmetry imposed by the choice of the centrosymmetric space group. Thus the Rh atom, C(1) (of form C), and its covalently bonded chlorine atom lie in the mirror plane which bisects the C(3)–C(4) (of form C) bond as well as the two double bonds of the co-ordinated cyclo-octadiene ligand.



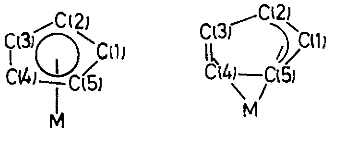
(1) (2)

(3)

FIGURE. ORTEP drawings for: $[(\eta^5\text{-}C_5Cl_5)Mn(CO)_5]$ (**1**), $[(\eta^5\text{-}C_5Ph_4Cl)Rh(C_2H_4)_2]$ (**2**), and $[(\eta^5\text{-}C_5Cl_5)Rh(1,5\text{-}C_8H_{12})]$ (**3**). All non-hydrogen atoms are represented by (50% probability) ellipsoids which reflect the refined anisotropic thermal parameters. Hydrogen atoms are shown only for $[(\eta^5\text{-}C_5Ph_4Cl]Rh(C_2H_4)_2]$ and are represented by arbitrarily small spheres for convenience.

The Table shows the presence of two short, 1·399(6) Å, and three long, 1·436(7,5,5) Å‡ C–C bonds within the η^5-bonded pentachlorocyclopentadienyl ring of (**3**) as well as three distinct classes of Rh–C(cyclopentadienyl) bond lengths resulting from a 4·6° folding of this ring about the C(2)–C(5) vector such that C(1) is brought closer to the metal atom [the corresponding angle of folding in (**2**) is 4·2°].

There are two classes of carbon–chlorine bond lengths: the C(1)–Cl bond length of 1·719(6) Å is 0·015 Å longer than the remaining four C–Cl linkages which average 1·704(5,2,2) Å. The latter distance agrees well with the average C–Cl bond length of 1·703 Å reported for decachlororuthenocene[4] and of 1·70(1) Å reported for chlorinated arenes. The longer C(1)–Cl bond length in (**3**) and the analogous C(1)–Cl distance of 1·721(5) Å in (**2**) reveals a departure from sp^2 hybridization for C(1), in the direction of the limiting value of 1·798(6) Å observed for the C(1)–Cl bond in (**1**) where C(1) has full sp^3 hybridization.



(A) (B) (C)

These observations are all consistent with a bonding model having a significant contribution from form (C). Although the crystal structure analysis of (**2**) showed some of these features,[3] all expected effects could not be observed since the cyclopentadienyl ring did not have five identical substituents and the bulky phenyl rings put additional constraints on the packing of the molecules into the three-dimensional lattice. The bonding parameters for the symmetrically substituted η^5-bonded cyclopentadienyl ring of (**3**) are intermediate between those for a symmetrically π-bonded ring with all bonds of a given type (C–C, Rh–C, or C–Cl) being essentially equivalent and those for the η^1-bonded pentachlorocyclopentadienyl ring in (**1**).[2] Three structural features common to (**2**) and (**3**) which may enhance the contribution of form (C) are: (i), possession of approximate (compound **2**) or rigorous (compound **3**) C_s molecular symmetry which results in removal of the metal orbital degeneracy (from essentially cylindrical symmetry as in the case of ferrocene) as well as the degeneracy of the bonding orbitals on the cyclopentadienyl ring;[1a] (ii), the chloro-substitution on the C(1) atom of the Cp ring; and (iii) the presence of five bulky substituents on the Cp ring. The effects we have observed involve all the bond lengths and the planarity of the $\eta^5\text{-}C_5Cl_5Rh$ unit. Similar localizations in unsubstituted systems have involved only the C–C parameters.[1]

We thank the Petroleum Research Fund administered by the American Chemical Society (V.W.D.) for support, the National Research Council of Canada for predoctoral (K.J.R.) and postdoctoral (A.S.) awards, and Professor H. C. Clark for his interest.

(*Received*, 13*th August* 1974; *Com.* 1041.)

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‡ The figures in parentheses following each averaged value are the r.m.s. value of the estimated standard deviation for an individual datum, and the mean and maximum deviation from the averaged value.

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