Crystal Structure and Location of the Bridging Hydride Ligand in μ-Chloro-μ-hydrido-bis[chloro-(pentamethylcyclopentadienyl)rhodium(III)], a Homogeneous Hydrogenation Catalyst

Melvyn Rowen Churchill* and Shirley Wei-Yang Ni

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. *Received October 14, 1972*

Abstract: The complex μ-chloro-μ-hydrido-bis[chloro(pentamethylcyclopentadienyl)rhodium(III)], $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$, crystallizes in the centrosymmetric orthorhombic space group *Pbcn* (D_{2h}^{14}; No. 60) with $a = 12.4879$ (14), $b = 14.4041$ (17), and $c = 12.8767$ (16) Å; $\rho_{obsd} = 1.67$ (1) and $\rho_{calcd} = 1.674$ g cm^{-3} for $M = 583.39$ and $Z = 4$. All atoms, including hydrogens, have been accurately located from an X-ray diffraction study based on counter data collected with a Picker FACS-1 diffractometer. The final discrepancy indices are $R_F = 5.78\%$ and $R_{wF} = 3.87\%$ for 1526 symmetry-independent reflections, representing data complete to $2\theta = 45°$ (Mo Kα radiation). The molecule has precise (crystallograpically dictated) C_2 symmetry, with a planar Rh(H)(Cl)Rh bridge. Interatomic dimensions include Rh···Rh = 2.906 (1), Rh–Cl(bridging) = 2.437 (2), Rh–Cl(terminal) = 2.393 (2), and Rh–H(bridging) = 1.85 (5) Å. Angles within the Rh(H)(Cl)Rh′ bridge are Rh–Cl–Rh′ = 73.20 (6), Rh–H–Rh′ = 103.6 (37), and H–Rh–Cl = H–Rh′–Cl = 91.6 (18)°.

For some time we have been concerned with transition metal derivatives in which hydride ligands bridge two or more metal atoms, and we have reported the results of X-ray diffraction studies on $HRe_2Mn(CO)_{14}$,[1] $[H_2Re_3(CO)_{12}^-]$,[2] $[H_6Re_4(CO)_{12}^{2-}]$,[3] $H_2Ru_6(CO)_{18}$,[4] and $H_6Cu_6[P(C_6H_5)_3]_6$.[5] While these studies have led, *inter alia*, to our suggesting[2,4] certain stereochemical principles whereby the most probable positions of μ_2- and μ_3-bridging hydride ligands may be ascertained, in none of these cases has the position of a bridging hydrogen atom been established directly from an electron density map. Other workers have had essentially similar experiences with such diverse species as $[HCr_2(CO)_{10}^-]$,[6] $[HFe_3(CO)_{11}^-]$,[7] $HRu_3(CO)_9(C_6H_5\cdot C\cdot C_6H_4)$,[8] $H_2Ru_3Fe(CO)_{13}$,[9] $HRu_3(CO)_9(C_{12}H_{15})$,[10] α-$H_2Ru_4(CO)_{13}$,[11] $HRh_3(\pi\text{-}C_5H_5)_4$,[12] and $HMo_2(CO)_4(\pi\text{-}C_5H_5)_2[P(CH_3)_2]$.[13] Only in $HMn_2(CO)_8[P(CH_3)_2]$[14] has a bridging hydride ligand been located from an electron density map and its position refined by least-squares methods (yielding Mn–H = 1.86 (6) Å and $\angle$(Mn–H–Mn) = 104 (5)°). Even here there are problems insofar as the final thermal parameter of the hydrogen atom is reported as -1.0 (2.5) Å^2; a negative value for this parameter is, of course, physically impossible.

We may note that an Mn–H–Mn bridge was also found from an electron density map of $HMn_3(BH_3)_2(CO)_{10}$;[15] the Mn–H distance has recently been reported as 1.65 (10) Å.[16]

We now report the crystal and molecular structure of $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$ in which we have been able to locate (and refine meaningfully by least-squares methods) all hydrogen atoms including that involved in a Rh–H–Rh bridge.

The molecule has additional chemical interest due to its activity as a catalyst in the homogeneous hydrogenation of olefins.[17]

Collection and Correction of the X-Ray Diffraction Data

The crystals have a dark red-brown appearance and give a deep cherry-red solution in ethyl acetate. A crystal was selected from a batch supplied by Professor P. M. Maitlis of McMaster University and was sealed into a thin-walled Lindeman glass capillary.

Preliminary (0–3)*kl* and *h*(0–3)*l* precession photographs (along with cone-axis photographs about the *a* and *b* directions) revealed the $D_{2h}(mmm)$ Laue symmetry of the reciprocal lattice, yielded approximate cell dimensions, and indicated the following systematic absences: 0*kl* for $k = 2n + 1$, *h*0*l* for $l = 2n + 1$, and *hk*0 for $h + k = 2n + 1$. These extinctions are consistent only with space group *Pbcn* [D_{2h}^{14}; No. 60].[18]

The crystal was approximately brick shaped, dimensions between principal faces being $(001) \rightarrow (00\bar{1}) = 0.316$, $(010) \rightarrow (0\bar{1}0) = 0.132$, and $(100) \rightarrow (\bar{1}00) = 0.0454$ mm; the crystal volume was 1.89×10^{-6} cm^3.

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Table I. Final Positional and Isotropic Thermal Parameters[a] for $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$, with Estimated Standard Deviations[b]

Atom	x	y	z	B, Å^2
Rh	0.033302 (26)	0.189613 (31)	0.141866 (36)	3.03
ClT	−0.14770 (13)	0.19821 (13)	0.08163 (13)	5.61
ClB	0	0.05376 (14)	1/4	4.64
C1	0.09334 (53)	0.20697 (45)	−0.01469 (47)	3.99
C2	0.10330 (54)	0.29063 (42)	0.04468 (51)	4.24
C3	0.17630 (49)	0.27184 (45)	0.12864 (50)	3.80
C4	0.20396 (48)	0.17604 (43)	0.12368 (46)	3.69
C5	0.15362 (53)	0.13737 (42)	0.03428 (49)	3.90
C6	0.03139 (91)	0.19688 (83)	−0.11329 (66)	5.98
C7	0.05605 (88)	0.38292 (62)	0.01521 (90)	6.23
C8	0.21727 (75)	0.34020 (58)	0.20614 (77)	5.31
C9	0.28034 (76)	0.12788 (72)	0.19299 (81)	5.05
C10	0.16527 (88)	0.04015 (62)	−0.00376 (80)	5.80
HB	0	0.2960 (53)	1/4	3.9 (16)
H6A	0.0524 (65)	0.2266 (71)	−0.1610 (61)	7.4 (26)
H6B	−0.0324 (57)	0.2106 (50)	−0.1137 (54)	4.6 (18)
H6C	0.0208 (79)	0.1238 (79)	−0.1329 (69)	10.8 (30)
H7A	0.0523 (59)	0.4243 (56)	0.0640 (58)	5.7 (21)
H7B	0.0898 (63)	0.4266 (59)	−0.0338 (62)	8.5 (20)
H7C	−0.0188 (69)	0.3710 (57)	−0.0112 (64)	7.6 (22)
H8A	0.2398 (77)	0.3170 (66)	0.2702 (65)	9.7 (28)
H8B	0.2778 (52)	0.3677 (42)	0.1897 (47)	4.4 (14)
H8C	0.1710 (48)	0.3897 (42)	0.2022 (47)	4.0 (13)
H9A	0.2687 (67)	0.0758 (58)	0.2007 (66)	7.2 (25)
H9B	0.3477 (71)	0.1329 (55)	0.1705 (61)	7.4 (22)
H9C	0.2918 (69)	0.1601 (59)	0.2535 (62)	8.0 (25)
H10A	0.2251 (62)	0.0420 (48)	−0.0547 (61)	7.8 (22)
H10B	0.1080 (59)	0.0250 (50)	−0.0477 (61)	6.7 (20)
H10C	0.1823 (60)	0.0010 (52)	0.0417 (61)	6.4 (21)

[a] "Equivalent isotropic thermal parameters" for nonhydrogen atoms correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid. [b] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and are derived from the inverse of the final least-squares matrix.

The crystal was transferred to a Picker FACS-1 automated diffractometer[19] and was accurately centered and aligned along its extended c^* direction. Unit cell dimensions (at 26°) obtained *via* a least-squares analysis of the resolved Mo Kα_1 (λ 0.70926 Å) components of 12 automatically centered high-angle (2θ = 29.2–48.8°) reflections are a = 12.4879 (14), b = 14.4041 (17), and c = 12.8767 (16) Å. The unit cell volume is 2316.2 Å^3. The observed density (ρ_{obsd} = 1.67 ± 0.01 g cm^{-3} by neutral buoyancy in aqueous zinc iodide solution) is consistent with that calculated for M = 583.39 and Z = 4 (ρ_{calcd} = 1.674 g cm^{-3}). In the absence of disorder the molecule has C_2 or C_i crystallographic symmetry imposed upon it.[18] Only the former (C_2) is consistent with the molecular formulation of Maitlis, *et al.*[17]

Intensity data were measured by executing a coupled θ–2θ (crystal:counter) scan from 0.6° in 2θ below the Kα_1 peak to 0.6° in 2θ above the Kα_2 peak at a rate of 1.0 deg/min, accumulating P counts in t_p sec. Stationary background counts, each 20 sec in duration, were measured at the low- and high-angle limits of the 2θ scan, giving B_1 and B_2 counts (respectively) for a total background counting time (t_B) of 40 sec. Copper foil attenuators, whose transmission factors for Mo Kα radiation had previously been accurately determined (and decreased the transmitted beam by successive factors of ~3–3.5), were automatically inserted as necessary to keep the maximum counting rate below 8500 counts/sec, thereby obviating possible coincidence losses.

A 3.0° takeoff angle to the X-ray source was employed; the detector aperture was ~4 × 4 mm with the detector 330 mm from the crystal.

Before collecting the data set, the intensity of a strong axial reflection (004) was measured (by a θ–2θ scan) at χ = 90° and at 10° intervals of ϕ from ϕ = 0 to ϕ = 360°. The observed 10% variation of intensity with ϕ was eliminated upon application of an absorption correction, thereby acting as an independent check on the validity of the absorption correction.

A unique data set having 0° < 2θ < 45° was gathered; a total of 1526 independent reflections was thus recorded. The intensities of three mutually orthogonal standard reflections were collected after every 50 reflections; root-mean-square deviations from the mean intensity were 0.78% for the 080, 0.91% for the 200, and 0.70% for the 004 reflection; these deviations were reduced only to 0.72, 0.88, and 0.64% (respectively) on applying a linear "decay" correction; and the crystal clearly was not disrupted significantly upon exposure to X-rays.

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated as follows.

$$I = q[(P + 4.5) - (t_p/t_B)(B_1 + B_2 + 9.0)]$$

and

$$\sigma(I) = q[(P + 4.5) + (t_p/t_B)^2(B_1 + B_2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

Here, the "ignorance factor" (p) was set equal to 0.04; q represents the combined corrections for crystal decomposition and attenuator used; and the numerical terms arise from the fact that the least significant digit of P, B_1, and B_2 is not recorded by the apparatus. Any negative I was reset to zero. All data were retained, none being rejected as "not significantly above background."

Unscaled structure factors amplitudes, F_o', and their standard deviations were calculated as $F_o' = (I/\mathrm{Lp})^{1/2}$, $\sigma(F_o') = [\sigma(I)/\mathrm{Lp}]^{1/2}$ for $\sigma(I) \geq I$, and $\sigma(F_o') = \{F_o' - [(F_o')^2 - \sigma(I)/\mathrm{Lp}]^{1/2}\}$ for $\sigma(I) < I$; here, the multiplicative Lorentz–polarization correction, 1/Lp, is given by $(2 \sin 2\theta)/(1 + \cos^2 2\theta)$.

Absorption corrections were calculated *via* the program DRAB, which was written by Dr. B. G. DeBoer; with μ = 18.8 cm^{-1}, the maximum and minimum transmission factors were 0.920 and 0.782.

Elucidation and Refinement of the Structure

Programs used include: FORDAP (Fourier synthesis, by A. Zalkin), SFIX (full-matrix least-squares refinement, derived *via* SFLS5, by C. T. Prewitt), STAN 1 (distances, angles, and their esd's, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral rhodium, chlorine, and carbon were taken from the table of Cromer and Waber;[20] those for hydrogen

(19) Exhaustive details of the apparatus and experimental procedure have appeared previously and will not be repeated here; see M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(20) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

Table II

(A) Anisotropic Thermal Parameters ($\times 10^5$)[a] for Nonhydrogen Atoms in the $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$ Molecule

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	500.2 (3.8)	341.6 (2.7)	475.3 (3.5)	24.6 (2.7)	14.6 (3.2)	11.6 (2.7)
ClT	757 (12)	809 (12)	812 (12)	74 (10)	−124 (11)	−38 (11)
ClB	905 (19)	435 (11)	704 (16)	0	42 (13)	0
C1	663 (51)	579 (42)	455 (43)	61 (39)	75 (41)	67 (34)
C2	720 (54)	467 (40)	658 (48)	15 (37)	39 (45)	152 (36)
C3	569 (46)	423 (33)	654 (48)	−109 (34)	148 (44)	61 (35)
C4	529 (42)	453 (37)	606 (47)	65 (36)	57 (39)	67 (34)
C5	682 (51)	452 (37)	558 (48)	57 (37)	104 (44)	35 (36)
C6	961 (86)	930 (73)	637 (65)	−99 (76)	−36 (66)	134 (54)
C7	1238 (104)	435 (47)	1109 (86)	64 (57)	−56 (77)	235 (56)
C8	766 (68)	484 (48)	1073 (79)	−147 (49)	−33 (67)	88 (50)
C9	656 (71)	601 (60)	915 (79)	80 (53)	−11 (58)	17 (55)
C10	1061 (87)	635 (55)	829 (76)	150 (58)	1 (72)	−200 (56)

(B) Root-Mean-Square Displacements (in Å) of Atoms along the Principal Axes of Their Vibration Ellipsoids[b]

Atom	$(\overline{U^2})^{1/2}_{min}$	$(\overline{U^2})^{1/2}_{med}$	$(\overline{U^2})^{1/2}_{max}$
Rh	0.187	0.197	0.205
ClT	0.229	0.268	0.298
ClB	0.214	0.241	0.269
C1	0.188	0.224	0.257
C2	0.194	0.236	0.260
C3	0.169	0.230	0.251
C4	0.195	0.208	0.243
C5	0.203	0.212	0.249
C6	0.224	0.270	0.323
C7	0.190	0.312	0.321
C8	0.202	0.261	0.305
C9	0.220	0.258	0.278
C10	0.216	0.279	0.309

[a] The anisotropic thermal coefficients enter the expression for the structure factor in the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. [b] The orientations of the atomic vibration ellipsoids are shown in the figures.

are from the compilation of Mason and Robertson.[21] The rhodium and chlorine values were corrected to allow for anomalous dispersion.[22]

A three-dimensional Patterson map was interpreted in terms of molecular C_2 symmetry and yielded the positions of the three independent "heavy" (*i.e.*, rhodium and chlorine) atoms. A Fourier synthesis, phased by these atoms, quickly led to the location of all remaining nonhydrogen atoms. Refinement of individual positional and isotropic thermal parameters led to convergence at $R_F = 8.6\%$ and $R_{wF} = 7.7\%$;[23] continued full-matrix least-squares refinement, now using anisotropic thermal parameters for all nonhydrogen atoms, converged to $R_F = 7.1\%$ and $R_{wF} = 6.2\%$. At this point data were corrected for the effects of the niobium filter on the initial background of low-angle reflections.[24] Only nine reflections were affected; two further cycles of refinement led to convergence with $R_F = 6.9\%$ and $R_{wF} = 6.2\%$. A difference-Fourier synthesis now revealed clearly the positions of all hydrogen atoms of the five methyl groups and the hydrogen atom that bridged the two rhodium atoms. This last atom, HB, corresponding to a peak at (0.00, 0.26, 0.25), had a peak height of 0.81 e Å^{-3} and was the second highest peak on the map. The highest peak (0.96 e Å^{-3} at 0.08, 0.22, 0.18) was only 0.85 Å from the rhodium atom and was ignored. Peak heights for methyl hydrogens ranged from 0.45 to 0.80 e Å^{-3}. Continued refinement by least-squares methods, with hydrogen atom positions and their isotropic thermal parameters also allowed to vary, led to final convergence at $R_F = 5.78\%$ and $R_{wF} = 3.87\%$. The highest feature on a final difference-Fourier synthesis was a peak of height 0.68 e Å^{-3} located about 0.7 Å from the rhodium atom position.

The observed structure factor amplitudes were inspected for evidence of extinction; none was found. The structural analysis was therefore declared complete. The final standard deviation of an observation of unit weight or "goodness-of-fit," defined by $[\Sigma w \cdot (|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.055, where the number of reflections (m) was 1526 and the number of refined parameters (n) was 176 (m/n = 8.7). The "goodness-of-fit" did not show any appreciable variation either as a function of $\sin\theta/\lambda$ or as a function of $|F_o|$.

A table of observed and calculated structure factor amplitudes is available.[25] Final positional and isotropic thermal parameters are collected in Table I; anisotropic thermal parameters are shown in Table II.

The Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table III; bond angles, with esd's, are given in Table IV. The overall stereochemistry of the molecule is illustrated in Figures 1 and 2.

As predicted by Maitlis and coworkers[17] the molecule consists of two $\pi\text{-}C_5(CH_3)_5RhCl$ units bridged by a chloride (ClB) and a hydride ligand (HB). The molecule has precise C_2 symmetry, with the twofold axis (at $x = 0$ and $z = 1/2$) running through the two bridging ligands. Half of the molecule, constituting the basic crystallographic "asymmetric unit," is numbered normally. Atoms in the remaining half of the molecule, which is related to the basic unit by the transformation ($-x$, y, $1/2 - z$), are labeled with a prime.

The diamagnetic molecule is best regarded as a derivative of rhodium(III), in which the arrangement of ligands about the metal ions may be described as quasi-octahedral (or, more graphically, as resembling a "three-legged piano stool"); see Figures 2 and 3.

(21) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, 2, 57 (1966).

(22) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 53, 1891 (1970).

(23) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w \cdot |F_o|^2]^{1/2}$.

(24) The rationale behind this correction and the method of application have been discussed in detail in a previous paper; see ref 19.

(25) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JACS-73-2150. Remit check or money order for $3.00 for photocopy or $2.00 for microfilm.

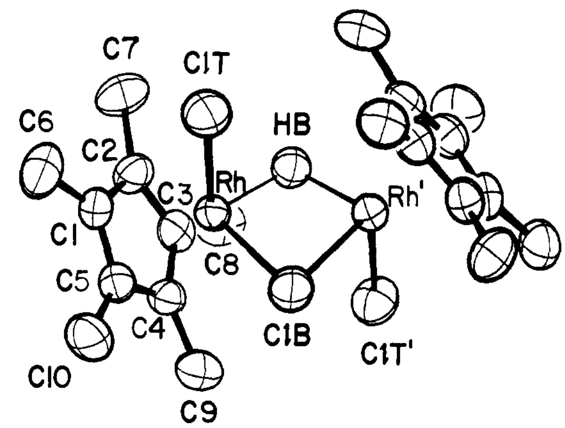


Figure 1. A general view of the $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$ molecule, with methyl hydrogen atoms omitted.

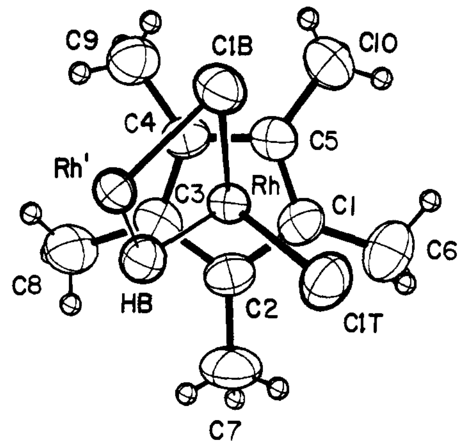


Figure 2. The asymmetric unit projected onto the plane of the cyclopentadienyl ring; atom Rh′ is also shown.

Table III. Intramolecular Distances (in Å) for $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$, with Estimated Standard Deviations[a]

Atoms	Dist	Atoms	Dist
(A) Distances from Rhodium Atom			
Rh–Rh′	2.9064 (10)	Rh–ClT	2.3929 (17)
Rh–HB	1.849 (47)	Rh–ClB	2.4374 (17)
Rh–C1	2.165 (6)	Rh···C6	3.287 (9)
Rh–C2	2.109 (6)	Rh···C7	3.239 (8)
Rh–C3	2.150 (6)	Rh···C8	3.266 (9)
Rh–C4	2.153 (6)	Rh···C9	3.277 (9)
Rh–C5	2.178 (6)	Rh···C10	3.297 (9)
Rh···Cp	1.777 (3)[b]		
(B) Carbon–Carbon Distances within π-$C_5(CH_3)_5$ Ligand			
C1–C2	1.433 (8)	C1–C6	1.494 (11)
C2–C3	1.440 (9)	C2–C7	1.503 (10)
C3–C4	1.424 (8)	C3–C8	1.492 (11)
C4–C5	1.425 (9)	C4–C9	1.479 (11)
C5–C1	1.403 (9)	C5–C10	1.491 (10)
C–C (av)	1.425	C–CH_3 (av)	1.492
(C) Carbon–Hydrogen Distances			
C6–H6A	0.79 (8)	C8–H8C	0.92 (6)
C6–H6B	0.82 (7)	C9–H9A	0.77 (8)
C6–H6C	1.09 (11)	C9–H9B	0.89 (8)
C7–H7A	0.87 (7)	C9–H9C	0.92 (8)
C7–H7B	0.99 (8)	C10–H10A	0.99 (7)
C7–H7C	1.01 (8)	C10–H10B	0.94 (7)
C8–H8A	0.93 (8)	C10–H10C	0.84 (7)
C8–H8B	0.88 (6)		
		C–H (av)	0.91

[a] Esd's are calculated by considering those elements of the full correlation matrix whose magnitudes are greater than 0.05. Calculation was performed using STAN 1, by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. [b] Cp is the centroid of the π-cyclopentadienyl ring.

Angles between the monodentate ligands are ClT–Rh–ClB = 93.76 (5)°, ClT–Rh–HB = 89.98 (13)°, and ClB–Rh–HB = 91.6 (18)°. From Cp (the centroid of the π-cyclopentadienyl ring), angles are Cp–Rh–ClT = 123.57 (10)°, Cp–Rh–ClB = 129.48 (10)°, and Cp–Rh–HB = 118.2 (14)°.

The distances of terminal and bridging chloride ligands from the rhodium atom vary by only about 0.045 Å, with Rh–ClT = 2.3929 (17) and Rh–ClB = 2.4374 (17) Å. The Rh–HB distance is 1.849 (47) Å (*vide infra*).

Individual rhodium–carbon (π-cyclopentadienyl) distances range from Rh–C2 = 2.109 (6) to Rh–C5 = 2.178 (6) Å, with a mean value of 2.151 Å. The Rh–Cp distance is 1.777 (3) Å. Within the carbocyclic five-membered ring carbon–carbon distances range from C5–C1 = 1.403 (9) to C2–C3 = 1.440 (9) Å, averaging 1.425 Å, while the carbon–methyl distances range from 1.479 (11) to 1.503 (10) Å, averaging 1.492 Å. (While few structural studies on π-pentamethyl-

Table IV. Interatomic Angles (deg) for $[\pi\text{-}C_5(CH_3)_5RhCl]_2HCl$[a]

Atoms	Angle	Atoms	Angle
(A) Angles about Rhodium Atom			
ClT–Rh–ClB	93.76 (5)	C1–Rh–C2	39.1 (2)
ClT–Rh–HB	89.98 (13)	C2–Rh–C3	39.5 (3)
ClB–Rh–HB	91.6 (18)	C3–Rh–C4	38.7 (2)
Cp–Rh–ClT[b]	123.57 (10)	C4–Rh–C5	38.4 (2)
Cp–Rh–ClB[b]	129.48 (10)	C5–Rh–C1	37.7 (2)
Cp–Rh–HB[b]	118.2 (14)		
(B) Angles about Bridging Ligands			
Rh–ClB–Rh′	73.20 (6)	Rh–HB–Rh′	103.6 (37)
(C) Internal Angles of the π-$C_5(CH_3)_5$ Ligand			
C(5)–C(1)–C(2)	108.3 (6)	C(3)–C(4)–C(5)	107.9 (5)
C(1)–C(2)–C(3)	107.3 (5)	C(4)–C(5)–C(1)	108.7 (5)
C(2)–C(3)–C(4)	107.6 (6)		
		Av	108.0
(D) External (C–C–CH_3) Angles of the π-$C_5(CH_3)_5$ Ligand			
C(5)–C(1)–C(6)	126.2 (7)	C(4)–C(3)–C(8)	125.9 (6)
C(2)–C(1)–C(6)	125.5 (7)	C(3)–C(4)–C(9)	125.7 (7)
C(1)–C(2)–C(7)	125.1 (7)	C(5)–C(4)–C(9)	126.1 (7)
C(3)–C(2)–C(7)	127.2 (7)	C(4)–C(5)–C(10)	126.1 (7)
C(2)–C(3)–C(8)	126.5 (6)	C(1)–C(5)–C(10)	125.2 (7)
		Av	126.0
(E) Angles Involving Hydrogen Atoms			
C1–C6–H6A	116 (6)	H6A–C6–H6B	101 (8)
C1–C6–H6B	119 (5)	H6A–C6–H6C	112 (8)
C1–C6–H6C	111 (5)	H6B–C6–H6C	96 (8)
C2–C7–H7A	116 (6)	H7A–C7–H7B	93 (7)
C2–C7–H7B	124 (5)	H7A–C7–H7C	108 (7)
C2–C7–H7C	107 (5)	H7B–C7–H7C	107 (7)
C3–C8–H8A	117 (6)	H8A–C8–H8B	97 (7)
C3–C8–H8B	116 (4)	H8A–C8–H8C	121 (7)
C3–C8–H8C	105 (4)	H8B–C8–H8C	100 (6)
C4–C9–H9A	114 (7)	H9A–C9–H9B	107 (9)
C4–C9–H9B	112 (6)	H9A–C9–H9C	114 (9)
C4–C9–H9C	112 (6)	H9B–C9–H9C	95 (8)
C5–C10–H10A	105 (4)	H10A–C10–H10B	100 (7)
C5–C10–H10B	110 (5)	H10A–C10–H10C	107 (7)
C5–C10–H10C	115 (6)	H10B–C10–H10C	117 (8)
Av	113	Av	105

[a] See footnote *a* to Table III. [b] Cp is the centroid of the π-cyclopentadienyl ring.

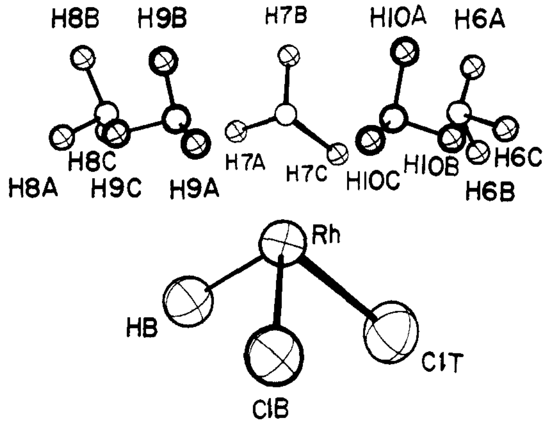


Figure 3. A side-on view of the asymmetric unit, illustrating the orientation of the hydrogen atoms of the methyl groups. (Carbon and hydrogen atoms of the five methyl groups are shown as artificial 0.1 Å spheres; the five carbon atoms of the carbocyclic ring have been omitted for the sake of clarity.)

cyclopentadienyl derivatives have been reported, the mean C–C(ring) distance in π-$C_5(CH_3)_5Fe(CO)_2SO_2CH_2\cdot CH{=}CH\cdot CH_3$[26] is 1.431 Å and the average C–CH_3 distance is 1.509 Å.)

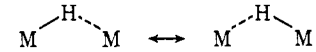
Carbon–hydrogen distances within the present molecule range from C9–H9A = 0.77 (8) to C6–H6C = 1.09 (11) Å; the average carbon–hydrogen distance is 0.91 Å. As usual, the X-ray determined C–H bond length is systematically (and significantly) shorter than the recognized internuclear C–H distance of 1.08 Å. This discrepancy arises from the use of a spherically symmetric scattering factor for the hydrogen atom when the true electron distribution is "pear shaped" with pronounced elongation in the direction of the hydrogen → carbon vector. Angles within the five-membered ring range from C(1)–C(2)–C(3) = 107.3 (5) to C(4)–C(5)–C(1) = 108.7 (5)°, with a mean of 108.0°—as expected for a planar regular pentagon. External C–C–CH_3 angles vary from 125.1 (7) to 127.2 (7)° with a mean of 126.0°. The carbon-atom skeleton of the π-$C_5(CH_3)_5$ ligand thus has fivefold symmetry within the limits of experimental error. The orientation of methyl groups is such that each presents a hydrogen atom pointing vertically upward on the outer side (*i.e.*, away from the metal atom) of the planar carbocyclic ring—see Figure 3.

Within the methyl groups C–C–H angles range from 105 (4) to 124 (5)° [av = 113°] and H–C–H angles range from 93 (7) to 121 (7)° [av = 105°]. These angles show no systematic errors but are of low accuracy because of the small contribution that a hydrogen atom makes to the total diffracting power of the crystal. (Even at $\theta = 0°$ each symmetry-independent hydrogen atom contributes only about 0.68% to the total scattering power of the crystal, since $Z(H)/\Sigma Z$ (asymmetric unit) = 1/146; at increasing angles of diffraction the percentage contribution decreases.)

The Bridging Hydride Ligand

The bridging hydride ligand, HB, was restricted in the least-squares analysis to lie on the crystallographic twofold axis at $x = 0$ and $z = {}^1/_2$. The essential isotropic appearance of this peak on the penultimate difference-Fourier map, coupled with results of the least-squares refinement process, lead us to believe that the hydride ligand does, indeed, lie on (or, at least, extremely close to) this axis. (The atom was well-behaved in the least-squares process and its parameters converged quickly to their final values. The last set of shifts were $\Delta y = 0.0000023$ and $\Delta B = 0.0141$ Å^2. The final thermal parameter, B(HB) = 3.9 (16) Å^2, is in good agreement with those of nearby atoms, *viz.*, B(Rh) = 3.03 and B(ClB) = 4.64 Å^2.)

Ibers and coworkers dealt with a similar situation in their structural study of $HMn_2(CO)_8[P(CH_3)_2]$[14] (in which, again, the molecule lies on a twofold axis) and agonized over the problem of attempting to distinguish between a symmetrical M–H–M bond (*i.e.*, single-minimum potential well) and a system in which there was a potential well with a double minimum (*i.e.*, a system in which a hydrogen atom is disordered about the twofold axis, and which can crudely be represented by I where the disorder could be either static or dynamic).



Ia Ib

Our study leads to the same point of equivocation, but we prefer a symmetric model. We may note that ^1H nmr studies show the hydride resonance as a triplet (τ 21.37, J_{Rh-H} = 23 Hz) with coupling due to two equivalent ^{103}Rh nuclei ($I = {}^1/_2$); infrared studies show a bond at 1151 cm^{-1} attributed to Rh–H–Rh, which is shifted to 812 cm^{-1} (ratio 1.41:1) upon deuteration.[17]

The Rh–H–Rh linkage is best regarded as consisting of a two-electron, three-center bond, which can be drawn (schematically) as II or III. The extent to

II III

which III is, in reality, important is directly related to the rhodium–rhodium distance. While we are unaware of any reported Rh(III)–Rh(III) bond distances, the present distance of 2.9064 (10) Å seems to be indicative of at least some metal–metal interaction. [For comparison, other Rh–Rh distances include the following: Rh(II)–Rh(II) = 2.936 (2) Å in $[(C_6H_5)_3P$-$(dmg)_2Rh]_2$ (dmg = dimethylglyoxime);[27] Rh(O)–Rh(O) = 2.78 in $Rh_6(CO)_{16}$,[28] 2.73 in $Rh_4(CO)_{12}$,[29] 2.62 in $[\pi$-$C_5H_5Rh(CO)]_3$,[30] and 2.68 in $(\pi$-$C_5H_5)_2$-$Rh_2(CO)_3$.[30]]

The small Rh–ClB–Rh angle of 73.20 (6)° also suggests significant metal–metal interaction, since M–Cl–M angles for square-planar or octahedral species are typically ~90°.

The Rh–HB–Rh′ angle of 103.6 (37)° is predominantly dictated by other restraints within the molecule. Using Pauling's value of 0.99 Å for the covalent radius of chlorine,[31a] our present Rh–ClT distance of 2.3929 (17) Å suggests 1.40 Å as the radius of rhodium(III) in the $[\pi$-$C_5(CH_3)_5RhCl]_2HCl$ molecule; a value of 0.30 Å for the covalent radius of hydrogen[31b] indicates that

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a Rh(III)–H(terminal) bond should be about 1.70 Å in length. This is consistent with available information, *viz.*, Rh(I)–H = 1.60 (12) Å in $HRh(CO)[P(C_6H_5)_3]_3$,[32] and Rh(III)–H = 1.48 (esd unspecified, but large) in $HRhCl(SiCl_3)[P(C_6H_5)_3]_2$.[33]

Our present value of Rh–H = Rh′–H = 1.849 (47) Å seems to be significantly greater than for terminal Rh–H bonds, although the estimated standard deviation is high. This result is expected and is in agreement with information available on diborane where terminal hydride ligands (H_t) are significantly closer to boron than the bridging ligands (H_b). [X-Ray diffraction results are B–B = 1.762 (10), B–H_t = 1.06 (2) and 1.09 (2), and B–H_b = 1.24 (2) and 1.25 (2) Å;[34] electron diffraction results are B–B = 1.775 (3), B–H_t = 1.196 (+0.008, −0.006), and B–H_b = 1.339 (+0.002, −0.006) Å;[35] spectroscopic results are B–B = 1.770 (5), B–H_t = 1.192 (10), and B–H_b = 1.329 (5) Å.[36]]

Finally we may note that positions of bridging hydride ligands determined from X-ray diffraction studies are not so prone to systematic errors as those of terminal hydride ligands since the deviations of the electron density from spherical symmetry in the former case act such as to conserve the same center of gravity (save for a small displacement perpendicular to the metal–metal vector).

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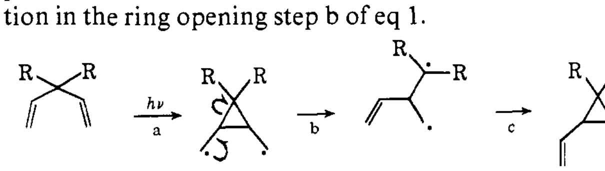
Accentuation of Di-π-methane Reactivity by Central Carbon Substitution. Mechanistic and Exploratory Organic Photochemistry. LXXV[1]

Howard E. Zimmerman,* Robert J. Boettcher, and Werner Braig

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received August 5, 1972*

Abstract: The photochemistry of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene was investigated to ascertain the effect of central phenyl substitution on the di-π-methane rearrangement. The synthesis of this tetraphenyl diene is described. The tetraphenyl diene was found to afford two products on direct irradiation, 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane and 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane. The first of these arises from the usual di-π-methane mechanism with vinyl–vinyl bonding as the initial excited state process. The second product results from phenyl–vinyl interaction. Phenyl–vinyl bridging selectively involves the vinyl group with the lower energy singlet excitation. The product structures were elucidated by nmr, mass spectral analysis, and degradation. The quantum efficiency on direct irradiation was determined as Φ = 0.076 for the 1,1,2,2-cyclopropane and Φ = 0.051 for the 1,1,2,3-cyclopropane. Sensitization with acetophenone gave none of the 1,1,2,3-cyclopropane but afforded the 1,1,2,2-cyclopropane much more efficiently, with a quantum yield of Φ = 0.42. Additionally, the sensitized runs yielded some 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, a product resulting from a new type of photochemical rearrangement. This was formed with an efficiency of Φ = 0.010. Thus, in the present di-π-methane system the triplet was quite reactive in contrast to previous acyclic cases. This is understood as a consequence of central phenyl substitution affecting the reactivity of a vinyl–vinyl bridged species along the reaction coordinate. An additional factor is inhibited energy dissipation as a result of steric hindrance preventing facile twisting of the excited vinyl groups. In the course of the research, a simple preparation of a high surface area support for efficient high-speed, high-pressure liquid chromatography was developed.

Previous extensive studies of the di-π-methane rearrangement[2] have focused attention both on cyclic and acyclic examples and established the very broad generality of the reaction. In most of the acyclic examples studied, there has been central methyl substitution on the methane carbon (*i.e.*, R = CH_3 in eq 1). It has been demonstrated[3] that the di-π-methane process is inefficient without such substitution. This was interpreted in terms of the need for odd-electron stabilization in the ring opening step b of eq 1.



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