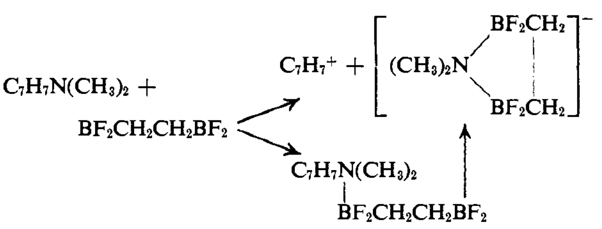
chelate adduct was also characterized by stoichiometric measurements (Table I). The adduct decomposes above 0° to a blue-green gum over a period of hours.

1,3,5-Cycloheptatrienyl-7-N,N-dimethylamine. A colorless precipitate is formed when this base reacts with 1,2-bis(difluoroboryl)ethane in hydrocarbon solvents. (Decomposition occurs very rapidly in methylene chloride, precluding the use of this solvent.) The ir spectrum of this product showed peaks characteristic of the tropenium ion as well as both trigonal and tetrahedrally coordinated boron. Upon standing overnight at 0° the tropenium ion and tetrahedral B–F bands were enhanced, and the trigonal B–F bonds were diminished in relative proportions (Figure 1); thus, it appears that the adduct is a mixture of 1:1 adducts. These compounds are related by the equations



(6)

Thus, as noted previously with the triphenylmethyl compounds, the chelation reaction of the N donor is much slower than the corresponding reaction of the O donor. Presumably, this phenomenon occurs since the amide ions, R_2N^-, are poorer leaving groups than the alkoxide ions, RO^-.[11] This effect is currently under further study.

[11] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 164.

Structural Characterization of a Tetranuclear Rhodium Complex, $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, Containing a Coordinate–Covalent Electron-Pair Rhodium(I)–Rhodium(III) Bond

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Abstract: The rhodacyclopentadiene complex $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, produced in the reaction of 3-hexyne with chlorodicarbonyl rhodium dimer, crystallizes with four molecules arranged in a triclinic unit cell of symmetry $B\bar{1}$ such that two half-molecules comprise the crystallographically asymmetric unit. The dimensions of this centrosymmetric B-centered cell are a = 16.78 Å, b = 20.45 Å, c = 9.60 Å, α = 96.4°, β = 89.5°, and γ = 102.7°. The structure consists of discrete $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ molecules in which two *cis*-tetraethylbutadiene fragments (each arising from the polymerization of two diethylacetylene molecules) are each coordinated to a Rh(III) by two σ bonds to give a rhodacyclopentadiene ring system and to a Rh(I) by two μ-type bonds. Two symmetrically bridging chlorine atoms interconnect each Rh(III) of a rhodacyclopentadiene ring to the Rh(I) which is not μ-bonded to that ring. Each Rh(I) has a localized square-planar environment through linkage with the midpoints of the two olefinic groups and the two chlorine atoms, while each Rh(III) has a localized square-pyramidal environment through bonding with the apical carbonyl group and with the two basal terminal diene-carbon and two chlorine atoms. The resulting molecular configuration, required to have a crystallographic center of symmetry, ideally conforms to C_{2h} symmetry. The unprecedented structural feature found in this complex is a coordinate–covalent Rh(I)–Rh(III) bond which is necessitated in order for each of the two centrosymmetrically related Rh(III) atoms per molecule to attain a coordinatively saturated electronic configuration. This proposed electron-pair metal-metal bond is in accord not only with the short Rh(I)–Rh(III) distance of 2.70 Å being similar to rhodium–rhodium distances in other organorhodium complexes (where molecular stabilization by Rh–Rh bonds is obvious), but also with the stereochemical similarity of this complex to ferracyclopentadiene complexes which also possess coordinate–covalent metal-metal bonds. The chemical implications of the two Rh(I)–Rh(III) bonds in the $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ molecule are discussed.

The reactions of metal carbonyls with acetylenes have resulted in a large variety of organometallic complexes with unusual structural features and novel types of bonding.[3–6] Maitlis, McVey, and Kang[6] found the reaction of diethylacetylene with chlorodicarbonylrho-

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[1] (a) University of Wisconsin; (b) McMaster University.

[2] This manuscript is based in part on the Ph.D. dissertation of L. R. B., University of Wisconsin, Jan 1969.

[3] M. L. H. Green, "Organometallic Compounds," Vol. 2, "The Transition Elements," Methuen and Co., London, 1968, pp 289–311, and references therein.

[4] W. Hübel, "Organic Synthesis *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, pp 273–342, and references therein.

[5] F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968).

[6] (a) P. M. Maitlis, S. McVey, and J. W. Kang, Proceedings of the First International Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, Italy, Sept 1968, D-2; (b) J. W. Kang, S. McVey, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3189 (1968), and references contained therein.

dium dimer in benzene at 80° to give as major products tetraethyl-*p*-benzoquinone, chloro(tetramethylcyclopentadienone)rhodium (which exists as a trimer in chloroform solution), and an extremely stable crystalline complex formulated as $Rh_4Cl_4C_{26}H_{40}O_2$.[7] An infrared spectrum of this latter complex, which does not thermally decompose below 400°, showed the presence of a strong terminal carbonyl band at 2025 cm^{-1} and no absorption bands in the region of an uncoordinated olefinic bond. Its nmr spectrum indicated the presence of two nonequivalent ethyl groups. The presumed phenyl analog, $Rh_4Cl_4C_{58}H_{40}O_2$, was also prepared by Maitlis and McVey[8] from the reaction of diphenylacetylene with chlorodicarbonylrhodium dimer in benzene. A product of the $LiAlH_4$ reduction of $Rh_4Cl_4C_{26}H_{40}O_2$ was determined to be 4,5-diethyloctane by its mass spectral cracking pattern, which thereby indicated the presence of a tetraethyl-substituted butadiene fragment in the $Rh_4Cl_4C_{26}H_{40}O_2$ complex.

Among the organoiron complexes isolated from the iron-carbonyl-acetylene reactions, several were shown from crystallographic characterization to possess a *cis*-butadiene fragment as part of a ferracyclopentadiene ring, *viz.*, $Fe(CO)_3(CH_3C_2OH)_2Fe(CO)_3$,[9] $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$,[10] and $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$.[11] Since no precedence based on structural evidence existed for complexes containing rhodacyclopentadiene rings, it was of particular interest to establish unambiguously the nature of the tetrarhodium complex $Rh_4Cl_4C_{26}H_{40}O_2$ and from the molecular geometry to formulate whether rhodium-rhodium interactions play an important role in the stabilization of these types of complexes.

Experimental Section

X-Ray Data Collection. Several of the parallelopiped-like purple crystals of $Rh_4Cl_4C_{26}H_{40}O_2$ were mounted in thin-walled Lindemann glass capillaries for X-ray examination. Preliminary Weissenberg and precession photographs indicated the crystals to be triclinic. A crystal of dimensions 0.18 × 0.18 × 0.12 mm with one of the 0.18-mm directions oriented along the rotation axis was used for the collection of Weissenberg intensity data; a second crystal of dimensions 0.25 × 0.25 × 0.15 mm with the spindle axis parallel to one of the 0.25-mm directions was used to obtain precession intensity data. Lattice lengths and two of the angles for a B-centered triclinic cell were obtained from *h0l* and *0kl* precession photographs calibrated by the superposition of a zero-layer NaCl exposure on the same film. The third triclinic angle was obtained both from an *hk0* Weissenberg photograph and from the difference of the spindle settings of the precession camera.

Equi-inclination Weissenberg data of reciprocal layers *hk0*–*hk*,10 of the B-centered triclinic cell were collected by the multiple-film technique with Zr-filtered Mo Kα radiation (λ 0.7107 Å). For all nonzero reciprocal levels two separate sets of data corresponding to a 360° rotation range were taken such that all independent reflections could be recorded on the upper half of the film packets. Relative intensities of each reflection were estimated visually by comparison with a set of timed standards prepared from the same crystal. Timed sets of precession data of the *nkl* and *hnl* (where *n* = 0, 1, and 2) reciprocal layers were taken with Mo Kα radiation, and the intensities measured by comparison with a standard set prepared in the same manner. The Weissenberg data were averaged and corrected for Lorentz-polarization effects[12] and spot-extension.[13] The Lp-corrected precession data were then merged with the Weissenberg data *via* a least-squares procedure[14] in order to place all data on a single scale. A weighted discrepancy factor of 5.6% was obtained in the merging of 1021 common reflections of the total 3265 independent reflections.[15] No absorption or extinction corrections were made. For Mo Kα radiation the linear absorption coefficient (μ) is 23.6 cm^{-1} for which the maximum intensity variation on a given reciprocal layer due to absorption was estimated[16] to be less than 12%. No anomalous dispersion corrections were applied to the scattering factors,[17] since their relatively small values[18,19] were presumed not to have any significant effect on the positional parameters in the centrosymmetric crystal.[20]

Crystal Data. The lattice constants for the B-centered triclinic cell are $a' = 16.78 \pm 0.02$ Å, $b' = 20.45 \pm 0.02$ Å, $c' = 9.60 \pm 0.02$ Å, $\alpha' = 96°22' \pm 10'$, $\beta' = 89°30' \pm 10'$, $\gamma' = 102°40' \pm 10'$. The reduced triclinic cell is related to the B-centered cell by the transformation[21] $a = {}^1/_2a' + {}^1/_2c'$, $b = {}^1/_2a' + b' + {}^1/_2c'$, $c = -c'$. The cell constants for the reduced cell are $a = 9.63 \pm 0.02$ Å, $b = 20.39 \pm 0.02$ Å, $c = 9.60 \pm 0.02$ Å, $\alpha = 97°\ 19' \pm 10'$, $\beta = 119°24' \pm 10'$, $\gamma = 96°02' \pm 10'$. A Delaunay reduction[22] showed no symmetry higher than triclinic. All results reported here are for the B-centered cell which was used for the structure determination. The density, measured by flotation in mixtures of ethyl iodide and 1,2-dibromoethane, was found to be 1.98 ± 0.04 g/cm³ as compared with a calculated value of 1.96 g/cm³ for four tetrarhodium species per unit cell. Normalized structure factors were calculated;[23] their statistical averages[24] of $\overline{|E|} = 0.806$, $\overline{|E^2|} = 0.984$, and $\overline{|E^2 - 1|} = 0.992$ indicated the centrosymmetric space group $B\bar{1}$. Thus, the structural determination required the location of four rhodium, four chlorine, two oxygen, and twenty-six carbon atoms.

Solution of Structure. The positions of the four independent rhodium atoms were located from an interpretation of a three-dimensional Patterson function.[25] Efforts to obtain initial coordinates for the other atoms from three-dimensional Fourier maps[25] phased on the heavy atom positions were unsuccessful. Two full-matrix least-squares cycles[26] on the positional parameters and isotropic temperature factors of the four rhodium atoms decreased the unweighted R_1 value[27] by 17% to a value of 27%. A three-dimensional Fourier difference map based on these refined rhodium parameters revealed the four chlorine positions. Preliminary positions of the other 28 atoms were then obtained from successive Fourier syntheses. The asymmetric unit was found to consist of two half-molecules, one of which was centered about the

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(7) *Anal.* Calcd for $Rh_4Cl_4C_{26}H_{40}O_2$: Rh, 43.88; Cl, 15.12; O, 3.41; C, 33.30; H, 4.30; mol wt, 938. Found:[6] Rh, 41.5; Cl, 14.67; O, 3.72; C, 33.53; H, 4.20; mol wt, 946 (determined osmometrically in chloroform solution).

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(9) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).

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(12) D. L. Smith, "Dacor—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

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(14) J. F. Blount, "Intav 3 and 4, A Program to Calculate Interlayer Structure Factors," University of Wisconsin, 1967.

(15) The standard deviation assigned to each merged reflection was $\sigma(\bar{F}) = [\Sigma_i K_i \sigma_i^2]^{1/2}$ where K_i is the *i*th scale factor; the individual standard deviations were calculated according to the relationships: $\sigma(F_o(hkl)) = 0.05F_o$ for $I_0(hkl) \geq \sqrt{10}I_{\min}$; $\sigma(F_o(hkl)) = 0.05F_o(hkl)(\sqrt{10}I_{\min}/I_0(hkl))^2$ for $I_0(hkl) < \sqrt{10}I_{\min}$.

(16) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

(17) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(18) For Mo Kα radiation $\Delta f' = -1.1$, $\Delta f'' = 1.2$ for Rh; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for Cl.[19]

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(25) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(26) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS—A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963.

(27) R_1 is defined as $\Sigma|F_o| - |F_c||/\Sigma|F_o|$ and R_2 is defined as equal to $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table I. Final Atomic Parameters with Standard Deviations[a]

Atom[b]	x	y	z	B
Rh(1)	1.0314 (1)	0.1045 (1)	0.0232 (1)	2.16 (3)
Rh(2)	1.0251 (1)	0.0151 (1)	0.2125 (1)	2.18 (3)
Rh(3)	0.7251 (1)	0.3954 (1)	0.2332 (1)	2.34 (3)
Rh(4)	0.8613 (1)	0.4848 (1)	0.1737 (1)	2.28 (3)
Cl(1)	1.0996 (4)	0.0705 (3)	−0.1999 (5)	2.5 (1)
Cl(2)	0.9087 (4)	0.7069 (3)	−0.1432 (5)	2.8 (1)
Cl(3)	0.6651 (4)	0.4295 (3)	0.4635 (5)	3.0 (1)
Cl(4)	0.5945 (4)	0.4232 (3)	0.1467 (5)	2.9 (1)
C(1T)	1.0609 (17)	0.1963 (12)	0.0253 (22)	3.3 (5)
O(1T)	1.0798 (14)	0.2557 (10)	0.0349 (19)	6.4 (5)
C(2T)	0.6989 (19)	0.3044 (14)	0.2218 (25)	4.1 (5)
O(2T)	0.6821 (14)	0.2453 (10)	0.2267 (19)	5.7 (5)
C(1R)	1.1167 (14)	0.0946 (10)	0.1576 (18)	2.1 (4)
C(2R)	1.1038 (14)	0.1086 (10)	0.3002 (19)	2.2 (4)
C(3R)	1.0230 (14)	0.1110 (10)	0.3252 (19)	2.3 (4)
C(4R)	0.9726 (13)	0.1031 (10)	0.2059 (18)	1.9 (3)
C(5R)	0.8341 (14)	0.4016 (10)	0.3026 (19)	2.3 (4)
C(6R)	0.8955 (13)	0.3890 (10)	0.2014 (17)	1.8 (3)
C(7R)	0.8647 (15)	0.3887 (11)	0.0570 (20)	2.5 (4)
C(8R)	0.7876 (15)	0.3992 (11)	0.0533 (20)	2.7 (4)
C(1E)	1.2024 (17)	0.0924 (12)	0.1018 (23)	3.6 (5)
C(1M)	1.2528 (21)	0.1624 (15)	0.0662 (28)	5.5 (7)
C(2E)	1.1721 (17)	0.1163 (12)	0.4179 (22)	3.6 (5)
C(2M)	1.1753 (20)	0.0448 (14)	0.4625 (27)	4.3 (6)
C(3E)	0.9903 (16)	0.1187 (11)	0.4756 (22)	3.3 (5)
C(3M)	0.9983 (15)	0.1945 (10)	0.5350 (19)	3.4 (4)
C(4E)	0.8704 (20)	0.0958 (15)	0.2065 (28)	5.0 (6)
C(4M)	0.8601 (19)	0.1692 (13)	0.1864 (26)	4.6 (6)
C(5E)	0.8582 (14)	0.4109 (11)	0.4583 (19)	2.7 (4)
C(5M)	0.8295 (16)	0.3397 (12)	0.5169 (23)	4.0 (5)
C(6E)	0.9857 (16)	0.3849 (12)	0.2434 (22)	3.8 (5)
C(6M)	1.0436 (17)	0.4566 (13)	0.2625 (24)	4.4 (5)
C(7E)	0.9243 (16)	0.3823 (11)	−0.0654 (21)	3.1 (4)
C(7M)	0.9144 (19)	0.3051 (13)	−0.1175 (25)	4.8 (6)
C(8E)	0.7384 (18)	0.4014 (13)	−0.0871 (23)	4.0 (5)
C(8M)	0.6900 (18)	0.3298 (14)	−0.1381 (26)	4.2 (6)

[a] Standard deviations of the last significant figures are enclosed in parentheses. [b] The different atoms are denoted by symbols as follows: T, terminal carbonyl carbon and oxygen atoms; R, rhodacyclopentadiene carbon atoms; E, methylene carbon atoms of the ethyl groups; M, methyl carbon atoms of the ethyl groups. For the crystallographically independent atoms comprising molecule 1, the rhodium and chlorine atoms are labeled 1 and 2, the carbonyl carbon and oxygen atoms are numbered 1, while the four rhodacyclopentadiene carbon atoms and corresponding ethyl group carbon atoms are designated 1 through 4. The atoms comprising the independent half of molecule 2 are labeled 3 and 4 for rhodium and chlorine atoms, 2 for the carbonyl carbon and oxygen atoms, and 5–8 for the rhodacyclopentadiene carbon atoms and the corresponding methylene and methyl carbon atoms.

center of symmetry at (0, 0, 0) and the other centered about the center of symmetry at ($^3/_4$, $^1/_2$, and $^1/_4$) of the B-centered cell.

Four cycles of full-matrix isotropic least squares based on the 1100 largest observed structure factors resulted in $R_1 = 9.4\%$ and $R_2 = 12.3\%$.[27] The extremely high thermal parameters from the last least-squares cycle for two of the originally chosen methyl carbon atoms indicated that their coordinates were not correct. A Fourier difference map based on the other 34 atoms of the asymmetric unit revealed the correct methyl positions. Three further cycles of least squares, in which all of the observed data were utilized, resulted in final discrepancy factors of $R_1 = 9.3\%$ and $R_2 = 10.2\%$. For all atoms except the ethyl carbon atoms, shifts of the positional parameters and temperature factors were less than $^1/_3$ their estimated error. Methyl carbons C(2M), C(3M), C(5M), and C(7M) had shifts of about 1.0σ on the average for the positional parameters and temperature factors; the largest shifts were for the z coordinate and temperature factor of C(3M) of 2.32σ and 1.84σ, respectively. Although some anisotropic motion of the rhodium and chlorine atoms was detected from the final difference map, no further refinement was carried out in that each isotropic least-squares cycle required 25 min of time on the CDC 3600 computer (and the additional expense was not considered to be justified by the increased precision). This Fourier difference map showed no residual electron density peaks or holes greater than 0.5 e/Å^3 except in the vicinity of the rhodium and chlorine atoms.

Positional and thermal parameters obtained from the output of the final isotropic least-squares cycle are listed in Table I.[28] Intramolecular distances and angles together with their standard deviations are listed in Table II. Table III gives the "best" least-squares planes for certain atoms as well as perpendicular distances of these and other atoms from the planes.

The Blount program[25] was used to calculate all Patterson and Fourier maps. The full-matrix least-squares refinement cycles were carried out with a locally modified version of the Busing–Martin–Levy OR FLS program.[26] Bond lengths and angles with standard deviations were calculated from the full inverse matrix (which included errors in lattice parameters) with the Busing–Martin–Levy OR FFE program.[29] The least-squares plane calculations were performed with the Smith program.[30]

Discussion

Description of the Structure. The compound $Rh_4Cl_4C_{26}H_{40}O_2$, whose configuration is shown in Figures 1 and 2, consists of discrete molecules arranged in the B-centered triclinic unit cell (Figure 3) such that two half-molecules comprise the crystallographically asymmetric unit. Of the four rhodium atoms per molecule, the two crystallographically independent ones are of two different types; one rhodium atom (which may be formally considered as a Rh(III)) is σ bonded to a tetraethyl-substituted *cis*-butadiene fragment to form a rhodacyclopentadiene ring. This ring in turn functions as a diolefin coordinating group by the formation of two μ-type bonds to the other independent rhodium atom (which may be considered as a Rh(I)). Two symmetrically bridging chlorine atoms also interconnect the Rh(III) of the rhodacyclopentadiene ring to the other

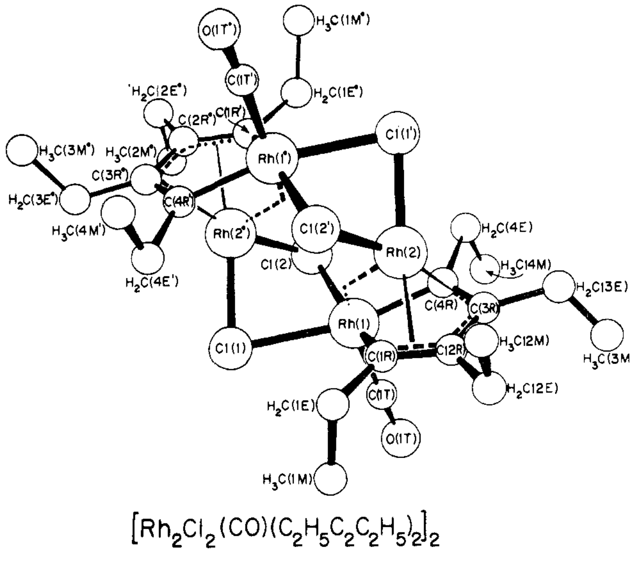

Figure 1. Molecular configuration of $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$.

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(28) A table containing observed and calculated structure factors has been deposited as Document No. NAPS-00693 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(29) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(30) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

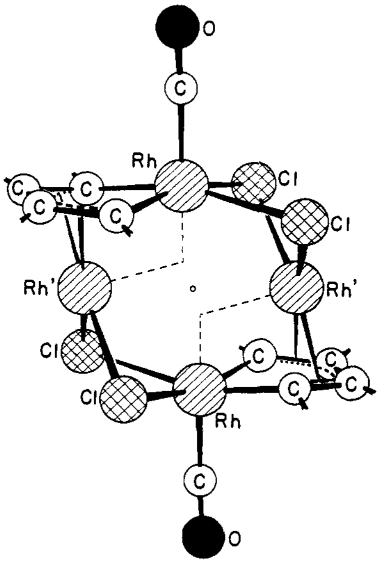

Figure 2. Geometry of the $[Rh_2Cl_2(CO)(C_2)_2]_2$ fragment (*i.e.*, without the ethyl groups).

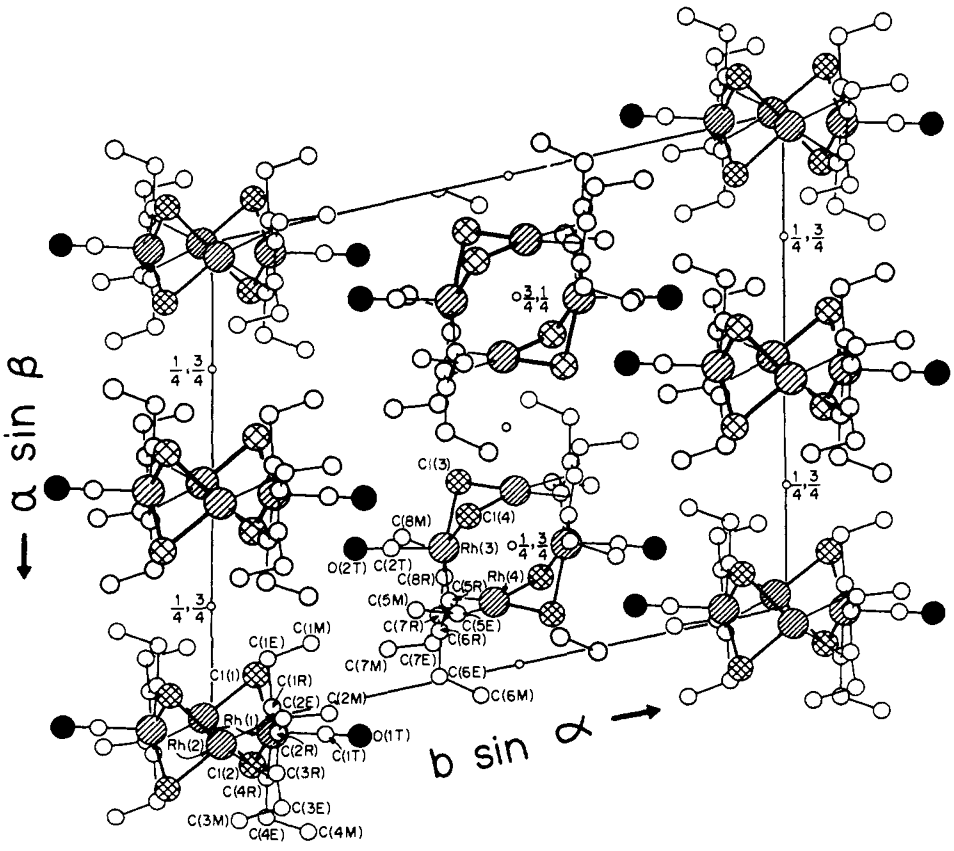

Figure 3. [001] projection of the B-centered triclinic unit cell of $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ showing the orientations of the four molecules per cell. Molecule 1 is located about the center of symmetry at (1, 0, 0), while molecule 2 is located about the center of symmetry at ($^3/_4$, $^1/_2$, $^1/_4$).

centrosymmetrically related Rh(I) atom to which the ring is *not* μ bonded. The plane of the four rhodium atoms in the molecule is perpendicular both to the plane of the four chlorine atoms and to the plane of the *cis*-butadiene fragment of the rhodacyclopentadiene ring.

The Rh(III) atom contained in the metallocyclopentadiene ring has a (square-pyramidal)-like arrangement of carbon and chlorine ligands about it. The two terminal carbon atoms of the *cis*-butadiene fragment and two bridging chlorine atoms occupy positions in the basal plane with the terminal carbonyl group located at the apical site. The Rh(III) is not coplanar with its four attached basal atoms but is displaced from this mean basal plane toward the Rh(III)–Co(terminal) bond direction. Each Rh(I) has a square-planar environment by its coordination with two bridging chlorine atoms and the midpoints of the two olefinic bonds of the metallocyclopentadiene group.

Although a center of inversion is the maximum symmetry imposed on the molecule by the crystallographic unit cell, the idealized geometry of the molecule excluding the methyl carbon atoms of the tetraethyl-substituted rhodacyclopentadiene rings is C_{2h}-2/m. The chemically equivalent bond lengths based on this symmetry differ from one another by less than 3σ. The mirror plane, which contains the four rhodium atoms and the two carbonyl carbon and oxygen atoms, bisects the two rhodacyclopentadiene rings and the four chlorine atoms in pairs; Table III ((7) and (8)) shows that the corresponding distances of the symmetry-related atoms to the mirror plane in each molecule are the same within 0.07 Å. Since the two crystallographically independent half molecules in the unit cell are equivalent within experimental error, all bond distances and angles reported in this discussion are the averaged values for the two molecules based on C_{2h} symmetry unless noted to the contrary.

The Rhodacyclopentadiene Ring. (a) The Rhodium(III)–Carbon Interaction. As found for other

Table II. Distances and Angles with Standard Deviations[a]

A. Intramolecular Distances, Å

		Av (a)	Av (b)			Av (a)	Av (b)
Rh–Rh distances				Rh(4)–C(5R)	2.18 (2)		
Rh(1)–Rh(2)	2.702 (3)						2.15
		2.699	2.699	Rh(2)–C(4R)	2.18 (2)		
Rh(3)–Rh(4)	2.696 (3)					2.16	
Rh(1)···Rh(2′)[b]	3.130 (3)			Rh(4)–C(8R)	2.13 (2)		
		3.141	3.141	Rh(2)–C(3R)	2.14 (2)		
Rh(3)···Rh(4′)	3.153 (3)					2.15	
Rh(1)···Rh(1′)	4.146 (5)			Rh(4)–C(7R)	2.16 (2)		
		4.149	4.149				2.16
Rh(3)···Rh(3′)	4.152 (5)			Rh(2)–C(2R)	2.16 (2)		
Rh(2)···Rh(2′)	4.122 (5)					2.18	
		4.138	4.138	Rh(4)–C(6R)	2.20 (2)		
Rh(4)···Rh(4′)	4.145 (6)			C(ring)–C(ring) distances			
Rh–Cl distances				C(1R)–C(2R)	1.39 (2)		
Rh(1)–Cl(1)	2.520 (6)					1.42	
		2.516		C(5R)–C(6R)	1.45 (3)		
Rh(3)–Cl(3)	2.513 (6)						1.40
			2.530	C(3R)–C(4R)	1.40 (3)		
Rh(1)–Cl(2)	2.541 (6)					1.38	
		2.544		C(7R)–C(8R)	1.36 (3)		
Rh(3)–Cl(4)	2.548 (7)			C(2R)–C(3R)	1.38 (3)		
Rh(2)–Cl(1′)	2.411 (6)					1.43	1.43
		2.416		C(6R)–C(7R)	1.48 (2)		
Rh(4)–Cl(3′)	2.420 (6)			C(ring)–CH_2 distances			
			2.412	C(1R)–C(1E)	1.54 (3)		
Rh(2)–Cl(2′)	2.418 (6)			C(5R)–C(5E)	1.53 (3)		
		2.408		C(2R)–C(2E)	1.59 (3)		
Rh(4)–Cl(4′)	2.398 (6)			C(6R)–C(6E)	1.59 (3)		
Rh–(CO) distances						1.56	
Rh(1)–C(1T)	1.83 (2)	1.82	1.82	C(3R)–C(3E)	1.54 (3)		
Rh(3)–C(2T)	1.81 (3)			C(7R)–C(7E)	1.55 (3)		
C–O distances				C(4R)–C(4E)	1.69 (4)		
C(1T)–O(1T)	1.18 (3)			C(8R)–C(8E)	1.60 (3)		
		1.18	1.18	CH_2–CH_3 distances			
C(2T)–O(2T)	1.19 (3)			C(1E)–C(1M)	1.57 (4)		
Rh–C (ring) distances				C(5E)–C(5M)	1.59 (3)		
Rh(1)–C(1R)	1.99 (2)			C(2E)–C(2M)	1.58 (4)		
		1.96		C(6E)–C(6M)	1.56 (3)		
Rh(3)–C(5R)	1.92 (2)					1.57	
			1.98	C(3E)–C(3M)	1.57 (3)		
Rh(1)–C(4R)	2.00 (2)			C(7E)–C(7M)	1.58 (3)		
		2.00		C(4E)–C(4M)	1.58 (4)		
Rh(3)–C(8R)	2.01 (2)			C(8E)–C(8M)	1.54 (4)		
Rh(2)–C(1R)	2.09 (2)						
		2.14					

B. Bond Angles, Deg

		Av (a)	Av (b)			Av (a)	Av (b)
Rh–Rh–Rh angles				Angles centered on			
Rh(2′)···Rh(1)–Rh(2)	89.7 (1)			Rh(1) and Rh(3)			
		89.8	89.8	Cl(1)–Rh(1)–C(1R)	97.8 (6)		
Rh(4′)···Rh(3)–Rh(4)	89.9 (1)					97.3	
Rh(1′)···Rh(2)–Rh(1)	90.3 (1)			Cl(3′)–Rh(3)–C(5R)	96.9 (6)		
		90.2	90.2				98.1
Rh(3′)···Rh(4)–Rh(3)	90.1 (1)			Cl(2′)–Rh(1)–C(4R)	99.0 (6)		
Rh–Cl–Rh angles						98.8	
Rh(1)–Cl(1)–Rh(2′)	78.8 (2)			Cl(4′)–Rh(3)–C(8R)	98.7 (7)		
		79.1		C(1T)–Rh(1)–C(1R)	97.5 (9)		
Rh(3)–Cl(3′)–Rh(4′)	79.4 (2)					95.6	
			78.9	C(2T)–Rh(3)–C(5R)	93.6 (11)		
Rh(1)–Cl(2′)–Rh(2′)	78.2 (2)						95.9
		78.6		C(1T)–Rh(1)–C(4R)	97.1 (9)		
Rh(3)–Cl(4′)–Rh(4′)	79.1 (2)					96.2	
Cl–Rh–Cl angles				C(2T)–Rh(3)–C(8R)	95.3 (10)		
Cl(1)–Rh(1)–Cl(2)	80.6 (6)			C(1T)–Rh(1)–Cl(2)	100.8 (8)		
		80.3	80.3			101.6	
Cl(3′)–Rh(3)–Cl(4′)	79.9 (7)			C(2T)–Rh(3)–Cl(4′)	102.5 (8)		
Cl(1′)–Rh(2)–Cl(2′)	85.3 (6)						101.2
		85.0	85.0	C(1T)–Rh(1)–Cl(1)	99.2 (7)		
Cl(3)–Rh(4)–Cl(4)	84.8 (7)					100.8	
Rh–C–O angles				C(2T)–Rh(3)–Cl(3′)	102.5 (10)		
Rh(1)–C(1T)–O(1T)	176.2 (19)			Rhodacyclopentadiene angles			
		175.2	175.2	C(1R)–Rh(1)–C(4R)	77.4 (8)		
Rh(3)–C(2T)–O(2T)	174.3 (21)					78.4	78.4

Table II (*Continued*)

B. Bond Angles, Deg

		Av (a)	Av (b)			Av (a)	Av (b)
C(5R)–Rh(3)–C(8R)	79.4 (8)			C(ring)–C(ring)–CH_2 angles			
Rh(1)–C(1R)–C(2R)	118 (2)			C(2R)–C(1R)–C(1E)	121 (2)		
		118		C(6R)–C(5R)–C(5E)	117 (2)		
Rh(3)–C(5R)–C(6R)	118 (1)					122	
			117	C(3R)–C(4R)–C(4E)	126 (2)		
Rh(1)–C(4R)–C(3R)	115 (2)			C(7R)–C(8R)–C(8E)	124 (2)		
		116		C(1R)–C(2R)–C(2E)	124 (2)		
Rh(3)–C(8R)–C(7R)	117 (2)			C(5R)–C(6R)–C(6E)	124 (2)		
C(1R)–C(2R)–C(3R)	111 (2)					125	
		110		C(4R)–C(3R)–C(3E)	122 (2)		
C(5R)–C(6R)–C(7R)	110 (2)			C(8R)–C(7R)–C(7E)	129 (2)		
			112	C(3R)–C(2R)–C(2E)	125 (2)		
C(4R)–C(3R)–C(2R)	116 (2)			C(7R)–C(6R)–C(6E)	126 (2)		
		114				123	
C(8R)–C(7R)–C(6R)	113 (2)			C(2R)–C(3R)–C(3E)	122 (2)		
Rh–C(ring)–CH_2 angles				C(6R)–C(7R)–C(7E)	118 (2)		
Rh(1)–C(1R)–C(1E)	118 (1)			C(ring)–CH_2–CH_3 angles			
		121		C(1R)–C(1E)–C(1M)	114 (2)		
Rh(3)–C(5R)–C(5E)	124 (2)			C(2R)–C(2E)–C(2M)	110 (2)		
			120	C(3R)–C(3E)–C(3M)	112 (2)		
Rh(1)–C(4R)–C(4E)	120 (2)			C(4R)–C(4E)–C(4M)	104 (2)		
		119				110	
Rh(3)–C(8R)–C(8E)	118 (2)			C(5R)–C(5E)–C(5M)	108 (2)		
				C(6R)–C(6E)–C(6M)	111 (2)		
				C(7R)–C(7E)–C(7M)	108 (2)		
				C(8R)–C(8E)–C(8M)	109 (2)		

C. Closest Nonbonding Intramolecular Distances, Å

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Cl(1)···Cl(2)	3.272 (10)	Cl(3)···Cl(4)	3.250 (7)	C(3R)···Rh(1)	2.89 (2)	C(7R)···Rh(3)	2.89 (2)
C(1T)···Cl(1)	3.34 (2)	C(2T)···Cl(4)	3.43 (3)	C(3R)···C(3M)	2.58 (3)	C(7R)···C(7M)	2.53 (3)
C(1T)···Cl(2)	3.40 (2)	C(2T)···Cl(3)	3.40 (3)	C(3R)···C(2E)	2.64 (3)	C(7R)···C(6E)	2.74 (3)
C(1T)···C(4R)	2.88 (3)	C(2T)···C(8R)	2.82 (3)	C(3R)···C(2M)	3.47 (4)	C(7R)···C(8E)	3.40 (3)
C(1T)···C(1R)	2.88 (3)	C(2T)···C(5R)	2.72 (3)	C(3R)···C(4E)	2.75 (4)	C(7R)···C(8M)	3.41 (4)
O(1T)···Rh(1)	3.01 (2)	O(2T)···Rh(3)	2.99 (2)	C(4R)···Cl(2)	3.47 (2)	C(8R)···Cl(4)	2.51 (3)
C(1R)···Cl(1)	3.42 (2)	C(5R)···Cl(3)	3.34 (2)	C(4R)···C(4M)	2.57 (4)	C(8R)···C(8M)	2.55 (3)
C(1R)···C(3R)	2.29 (3)	C(5R)···C(7R)	2.41 (3)	C(4R)···C(3E)	2.58 (2)	C(8R)···C(7E)	2.63 (4)
C(1R)···C(4R)	2.50 (3)	C(5R)···C(8R)	2.51 (3)	C(4R)···C(3M)	3.47 (2)	C(8R)···C(7M)	3.46 (4)
C(1R)···C(1M)	2.60 (4)	C(5R)···C(5M)	2.52 (3)	C(1E)···Rh(1)	3.04 (3)	C(5E)···Rh(3)	3.06 (2)
C(1R)···C(2E)	2.63 (3)	C(5R)···C(6E)	2.69 (4)	C(1E)···Rh(2)	3.28 (3)	C(5E)···Rh(4)	3.26 (2)
C(1R)···C(2M)	3.42 (3)	C(5R)···C(6M)	3.48 (4)	C(1E)···C(2E)	3.07 (3)	C(5E)···C(6E)	3.05 (3)
C(2R)···Rh(1)	2.92 (2)	C(6R)···Rh(3)	2.90 (2)	C(2E)···Rh(2)	3.35 (2)	C(6E)···Rh(4)	3.34 (3)
C(2R)···C(4R)	2.36 (3)	C(6R)···C(8R)	2.37 (3)	C(2E)···C(3E)	3.10 (4)	C(6E)···C(7E)	3.14 (3)
C(2R)···C(2M)	2.60 (4)	C(6R)···C(6M)	2.60 (3)	C(2M)···Rh(2)	3.40 (3)	C(6M)···Rh(4)	3.37 (3)
C(2R)···C(1E)	2.55 (3)	C(6R)···C(5E)	2.55 (3)	C(3E)···C(4E)	3.22 (4)	C(7E)···C(8E)	3.24 (4)
C(2R)···C(1M)	3.43 (4)	C(6R)···C(5M)	3.40 (3)	C(4E)···Rh(1)	3.19 (3)	C(8E)···Rh(3)	3.09 (2)
C(2R)···C(3E)	2.56 (3)	C(6R)···C(7E)	2.60 (3)	C(4E)···Rh(2)	3.37 (3)	C(8E)···Rh(4)	3.32 (2)
C(2R)···C(3M)	3.42 (3)	C(6R)···C(7M)	3.39 (3)	C(4E)···Cl(2)	3.41 (3)	C(8E)···Cl(4)	3.35 (3)

[a] The average values in column a are the mean of the two independent molecules; average values in column b are means based on C_{2h} molecular symmetry of the $[Rh_2Cl_2(CO)(C_2)_2]_2$ fragment (*i.e.*, without ethyl groups). Standard deviations of the last significant figures are enclosed in parentheses. [b] The primed numbers refer to the atom transformed by the appropriate center of symmetry of the molecule.

metallocyclopentadiene complexes,[9,11,31,32] the *cis*-butadiene fragment of the rhodacyclopentadiene ring is planar within experimental error. The two chlorine atoms bonded to the rhodium(III) atom of this heterocyclic ring are also contained in this diene–carbon plane as are the methylene carbon atoms of the ethyl groups attached to each of the butadiene carbon atoms. The perpendicular displacement of the Rh(III) by 0.38 Å from the mean plane of its four attached chlorine and terminal diene–carbon atoms in the direction of the terminal carbonyl group is greater than the corresponding perpendicular displacement of the iron atom from its mean basal plane of four carbon atoms in $Fe(CO)_3(CH_3C_2OH)_2Fe(CO)_3$ (0.18 Å),[9] $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ (0.11 Å),[11] $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ (0.26 Å),[31] and $Fe_3(CO)_{10}(C_2H_2)_5$ (0.21 Å).[32] The rhodium(III)-to-(terminal diene–carbon) σ bond length of 1.99 Å (average) compares well with the corresponding iron-to-(terminal diene–carbon) distances in ferracyclopentadiene rings—*cf.* the black isomer $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ (2.031, 2.063 Å);[10] $Fe(CO)_3(CH_3C_2OH)_2Fe(CO)_3$ (1.94, 1.95 Å);[9] $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ (1.97, 1.98 Å);[11] and $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ (1.96 Å).[31] These distances are all shorter than the corresponding rhodium-to-(terminal diene–carbon) bond distance of 2.15 Å in the butadiene portion of the hexakis(trifluoromethyl)benzene part of $Rh(C_5H_5)[C_6(CF_3)_6]$.[33]

(b) The *cis*-Butadiene Fragment. Although two independent half-molecules of $[Rh_2Cl_2(CO)(C_2H_5C_2-$

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[31] E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, in press.

[32] C. E. Strouse and L. F. Dahl, submitted for publication.

[33] M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **292**, 61 (1966).

Table III. Equations of Best Molecular Planes with Distances (Å) of Atoms from These Planes

A. Equations of Best Planes[a]

(1) Plane Formed by Cl(1), Cl(2), C(1R), and C(4R)
$0.0236X + 0.9989Y - 0.0404Z - 2.1095 = 0$

Rh(1)	0.338	C(2R)	0.05
Cl(1)	0.016	C(3R)	0.02
Cl(2)	−0.016	C(4E)	0.05
C(1R)	−0.021	C(2E)	0.05
C(4R)	0.020	C(3E)	−0.06
Rh(2)	−1.71	C(4E)	−0.16
C(1T)	2.17	*i*(1, 0, 0)	−1.71
O(1T)	3.34		

(2) Plane Formed by Cl(3), Cl(4), C(5R), and C(8R)
$-0.1313X - 0.9909Y - 0.0296Z + 9.3306 = 0$

Rh(3)	0.328	C(6R)	0.05
Cl(3)	−0.078	C(7R)	0.01
Cl(4)	0.017	C(5E)	−0.09
C(5R)	0.022	C(6E)	−0.04
C(8R)	−0.022	C(7E)	−0.09
Rh(4)	−1.733	C(8E)	−0.06
C(2T)	2.12	$i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	−1.72
O(2T)	3.30		

(3) Plane Formed by Rh(2), Cl(1′), Cl(2′), M12,[b] and M34
$-0.1671X + 0.2011Y - 0.9652Z + 4.7706 = 0$

Rh(2)	−0.036	C(1R)	0.60
Cl(1′)	−0.024	C(2R)	−0.64
Cl(2′)	−0.006	C(3R)	−0.64
M12	0.035	C(4R)	0.59
M34	−0.016	*i*(1, 0, 0)	1.97
Rh(1)	2.16		

(4) Plane Formed by Rh(4), Cl(3′′), Cl(4′′), M56, and M78
$0.9311X + 0.1336Y - 0.3395Z - 12.0976 = 0$

Rh(4)	0.051	C(5R)	−0.67
Cl(3′′)	−0.036	C(6R)	0.64
Cl(4′′)	0.010	C(7R)	0.64
M56	−0.051	C(8R)	−0.57
M78	0.026	$i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	−1.96
Rh(3)	−2.14		

(5) Plane Formed by C(1R), C(2R), C(3R), and C(4R)
$0.0274X + 0.9972Y - 0.0695Z - 2.1192 = 0$

C(1R)	−0.009	C(1E)	0.08
C(2R)	0.016	C(2E)	0.00
C(3R)	−0.016	C(3E)	−0.14
C(4R)	0.009	C(4E)	−0.18
Rh(1)	0.38	Rh(2)	−1.72

(6) Plane Formed by C(5R), C(6R), C(7R), and C(8R)
$-0.1605X - 0.9862Y - 0.0395Z + 9.6559 = 0$

C(5R)	−0.002	C(5E)	−0.138
C(6R)	0.003	C(6E)	−0.134
C(7R)	−0.003	C(7E)	−0.125
C(8R)	0.002	C(8E)	0.00
Rh(3)	0.36	Rh(4)	−1.74

(7) Plane Formed by Rh(1), Rh(1′), Rh(2), and Rh(2′)
$0.9837X - 0.0098Y - 0.1795Z - 16.5046 = 0$

C(1T)	0.06	C(1R)	1.24
O(1T)	0.08	C(4R)	−1.26
Cl(1)	1.64	C(2R)	0.73
Cl(2)	−1.63	C(3R)	−0.66
M12	0.96		
M34	−1.00		

(8) Plane Formed by Rh(3), Rh(3′), Rh(4), and Rh(4′)
$-0.3459X + 0.0643Y - 0.9361Z + 5.1912 = 0$

C(2T)	0.00	C(5R)	−1.24
O(2T)	−0.12	C(8R)	1.27
Cl(3)	−1.63	C(6R)	−0.72
Cl(4)	−1.62	C(7R)	0.76
M56	−0.97		
M78	1.02		

(9) Plane Formed by Cl(1), Cl(1′), Cl(2), and Cl(2′)
$-0.1311X - 0.7077Y - 0.6942Z + 2.1994 = 0$

Rh(1)	−1.62	Rh(2)	−1.51

(10) Plane Formed by Cl(3), Cl(3′), Cl(4), and Cl(4′)
$0.5941X - 0.7521Y - 0.2854Z + 1.8250 = 0$

Rh(3)	1.63	Rh(4)	1.52

B. Appropriate Angles (Deg) between Normals to Planes

1-3	76.4	2-10	47.5	2-4	104.2	7-9	89.8
1-5	1.7	3-5	74.8	2-6	1.8	8-10	89.2
1-7	88.8	4-6	105.5	2-8	89.5	9-10	49.3
1-9	133.0	7-8	100.0				

C. Angles (Deg) between Vector and Normal to the Plane

Vector	Plane	Angle	Vector	Plane	Angle
Rh(1)–*i*(1,0,0)	1	8.5	$\mathrm{Rh(4)}–i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	2	90.4
Rh(1)–*i*(1,0,0)	3	84.7	$\mathrm{Rh(4)}–i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	4	13.8
$\mathrm{Rh(3)}–i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	2	9.3	Rh(1)–C(1T)	1	176.8
$\mathrm{Rh(3)}–i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$	4	94.8	Rh(1)–C(1T)	3	100.5
Rh(2)–*i*(1,0,0)	1	90.0	Rh(3)–C(2T)	2	173.3
Rh(2)–*i*(1,0,0)	3	13.7	Rh(3)–C(2T)	4	82.5

[a] The equations of these planes are given in orthogonal Å coordinates which are related to triclinic coordinates by the equations: $X = axt + b\cos\gamma\, yt + c\cos\beta\, zt$, $Y = b\sin\gamma\, yt + c\cos\mu\, zt$, $Z = c\cos\nu\, zt$, where $\cos\mu = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$ and $\cos\nu = (1 - \cos^2\beta - \cos^2\mu)^{1/2}$. Unit weights were used for all atoms forming the plane. [b] M12 is the midpoint of C(1R)–C(2R), M34 is the midpoint of C(3R)–C(4R), M56 is the midpoint of C(5R)–C(6R), and M78 is the midpoint of C(7R)–C(8R). The centers of symmetry for molecules 1 and 2 are *i*(1, 0, 0) and $i({}^{3}/_{4}, {}^{1}/_{2}, {}^{1}/_{4})$, respectively.

$C_2H_5)_2]_2$ in the unit cell have the same general configuration and a good agreement is found between the corresponding bond lengths and angles involving the rhodium and chlorine atoms of the two molecules, there is some variation of the butadiene carbon–carbon bond lengths in the two half-molecules. No unusual intermolecular packing effects appear to be the cause of these differences. Nevertheless, the average values based on chemical equivalence of the two independent half-molecules with C_{2h} molecular symmetry are 1.40 Å for the (terminal carbon)–(central carbon) bond length and 1.43 Å for the (central carbon)–(central carbon) bond length. These average values, which compare well with similar values in the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ (1.457 and 1.456 Å),[10] $Fe(CO)_3(CH_3C_2OH)_2Fe(CO)_3$ (1.418 and 1.430 Å),[9] and $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)Fe(CO)$ (1.38 and 1.42 Å),[11] suggest in accord with the approximate coplanarity of the substituent methylene carbon atoms with the diene–carbon atoms (Table III, (1) and (2)) that none of the four carbon atoms in the *cis*-butadiene system are markedly distorted from a trigonal-like sp^2 geometry on complexation by μ bonding with the Rh(I).

(c) The Rhodium(III)–Carbonyl Interaction. The carbonyl group bonded to the rhodium(III) atom is essentially perpendicular to the plane of the four atoms attached to the Rh(III). The Rh(III)–CO vector forms an average angle of 99° with the normal of the basal plane containing the Rh(I). The degree of displacement of the Rh(III) from its mean basal plane of two chlorine and two carbon atoms toward the carbonyl group is evidenced by the obtuse OC–Rh(III)–C(butadiene) angle of 96° and the obtuse OC–Rh(III)–Cl angle of 101°. The Rh–CO bond length of 1.82 Å compares well with the Rh–CO(terminal) distances in other rhodium carbonyl complexes.[34,35] The Rh–C–O angle of 175 ± 2° is essentially linear.

(d) The Relationship of Rh(I) to the Coordination Sphere of Rh(III). In order for each of the Rh(III) atoms of d^6 electronic configuration in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ to be considered as coordinatively saturated,[36] it is necessary to postulate a coordinate–covalent Rh(III)–Rh(I) bond with the Rh(I). If a bent metal–metal bond is assumed, the coordination site corresponding to the intersection of the appropriate Rh(I) and Rh(III) orbitals results in a localized octahedral-like environment about the Rh(III) and a square-pyramidal environment about the Rh(I).

The Rh_2Cl_2 Fragment. As in $[RhCl(CO)_2]_2$[37] and $[Rh(Cl)(C_2H_4)_2]_2$[38] the rhodium–chlorine framework in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is also bent; the plane formed by the Rh(I) and the two chlorine atoms forms an angle of 115.6° with the plane containing the Rh(III) atom and the same two chlorine atoms. This value is the same as that found in $[RhCl(C_2H_4)_2]_2$ (115.8°)[38] but less than the corresponding value in $[RhCl(CO)_2]_2$ (124°).[37] The average Rh(I)–Cl distance of 2.41 Å in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is similar to the Rh(I)–Cl distances in $[RhCl(CO)_2]_2$ (2.35 Å),[37] $[RhCl(C_8H_{12})_2]_2$ (2.38 Å),[39] and $[RhCl(C_2H_4)_2]$ (2.40 Å).[38] The longer average Rh(III)–Cl distance of 2.53 Å in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is not unlike the corresponding distances in the bis-π-allyl rhodium chloride dimer of 2.511 ± 0.004 and 2.469 ± 0.004 Å.[40]

Although the Rh_2Cl_2 fragments in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, $[RhCl(CO)_2]_2$,[37] and $[RhCl(C_2H_4)_2]_2$[38] are bent while that in $[RhCl(C_8H_{12})_2]_2$ is planar, in all four molecules the Cl···Cl nonbonding distances of 3.26, 3.25, 3.21, and 3.22 Å, respectively, are similar. The presumably nonbonding Rh(I)···Rh(III) distance of 3.14 Å in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is in the same range as the Rh(I)···Rh(I) distance in $[RhCl(CO)_2]_2$ (3.12 Å)[37] and $[RhCl(C_2H_4)_2]_2$ (3.02 Å),[38] for which weak metal–metal interactions are proposed, but is considerably less than the nonbonding Rh···Rh distance in $[RhCl(C_8H_{12})_2]_2$ of 3.50 Å.[39] The Rh–Cl–Rh angle of 79° in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is similar to that of 78° in $[RhCl(C_2H_4)_2]_2$[38] and 83° in $[RhCl(CO)_2]_2$[37] but is significantly smaller than the angle of 94° in $[RhCl(C_8H_{12})_2]_2$.[39] Due to the longer Rh(III)–Cl distances, the Cl–Rh(III)–Cl angle of 80° in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is not only less than the Cl–Rh(I)–Cl angle of 85° in this same molecule but also is less than the Cl–Rh(I)–Cl angles of 85° in $[RhCl(CO)_2]_2$,[37] 84° in $[RhCl(C_2H_4)_2]_2$,[38] and 85° in $[RhCl(C_8H_{12})_2]_2$.[39]

The Rhodium(I) Interaction with the Rhodacyclopentadiene Ring. The average distance of Rh(I) to the carbon atoms in the butadiene fragment of $[Rh_2Cl_2(CO)C_2H_5C_2C_2H_5)_2]_2$ is 2.14 Å for the terminal diene–carbon atoms and 2.17 Å for the central diene–carbon atoms. The perpendicular distance of Rh(I) from the mean butadiene plane is 1.73 Å. These average Rh(I)–Cl distances are slightly shorter than the average Rh–C(cyclopentadienyl) distances found in $Rh_3(C_5H_5)_3(CO)_3$ (isomer I) (2.24 Å),[41] $Rh_3(C_5H_5)_3(H)(C_5H_5)$ (2.23 Å),[42] $Rh_2(C_5H_5)_2(CO)_3$ (2.26 Å av),[35] and in $Rh(C_5H_5)[C_6(CF_3)_6]$ (2.20 Å)[33] as well as the average Rh(I)–C(butadiene) distance in $RhCl(C_4H_6)_2$ (2.20 Å).[43] The distances of Rh(I) from the mean carbon plane in the above rhodium cyclopentadienyl complexes are 1.90 Å (av), 1.90 Å (av), 1.88 Å (av), and 1.85 Å, respectively. The shorter Rh–C distances in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ should not necessarily be attributed to a stronger Rh–butadiene bond. The geometrical requirements of this tetranuclear rhodium complex, particularly the orthogonality of the two basal planes containing the two different kinds of rhodium atoms and the short Rh(I)–Rh(III) distance (see following section), may dictate this decrease of the metal-to-ring distance.

The Rh(I)–Rh(III) Interaction. The Rh(I)–Rh(III) interaction in this tetranuclear rhodium complex, $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, is the first known for any rhodium compound. Our proposal for a coordinate–covalent metal–metal bond between each of the two pairs of Rh(I) and Rh(III) atoms per molecule is based on the stereochemical similarity of $[Rh_2Cl_2(CO)_2(C_2H_5C_2C_2H_5)_2]_2$ to the related iron and osmium metallocyclopentadiene complexes (which possess coordinate–covalent metal–metal bonds) as well as on the resemblance of the Rh(I)–Rh(III) distance to the Rh–Rh bonding distances in other polynuclear rhodium complexes which are stabilized by Rh–Rh bonds.

The ferracyclopentadiene ring complexes studied by X-ray diffraction include $Fe(CO)_3(CH_3C_2OH)_2Fe(CO)_3$,[9] $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$,[44] $Fe_3(CO)_{10}(C_2H_2)_5$,[32] the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$,[10] $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$,[11] and $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$.[31] In these molecular compounds the ferracyclopentadiene ring is coordinated either to at least one tricarbonyl fragment or to an electronically equivalent Fe(CO)(cyclobutadiene) or Ni(cyclobutadiene) system *via* both a (*cis*-butadiene)–metal interaction and a metal–metal electron-pair bond. The corresponding dinuclear osmium analog $Os(CO)_3(HC_2CH_3)_2Os(CO)_3$ contains an osmacyclopentadiene ring linked to an osmium tricarbonyl fragment by an Os–Os bond as well as by the (*cis*-butadiene)–osmium

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interaction.[45] In these complexes a closed-shell electronic configuration is achieved for each metal atom by a formal contribution of two electrons from the nonring metal (considered to be zerovalent) to the ring metal (in an Fe(II) or Os(II) oxidation state) thereby resulting in a coordinate–covalent metal–metal bond. The Rh(III) atom in each of the two metallocyclopentadiene rings of the $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ molecule will similarly conform to a closed-shell configuration by formal donation of two electrons from the Rh(I) μ bonded to this same rhodacyclopentadiene ring. The nonring Rh(I) atom has the expected electron count of two less than a closed-shell configuration.

The bonding Rh(I)–Rh(III) distance of 2.699 Å in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ is consistent with the Rh–Rh distance in the metal (2.695 Å)[46] and is in the same range as the Rh–Rh bonding distances in other polynuclear rhodium systems for which electron-pair Rh–Rh bonds are necessary to account for the compounds' diamagnetism as well as stability; these complexes include $Rh_3(C_5H_5)_3(CO)_3$ (isomer I) (2.62 Å),[41] $Rh_3(C_5H_5)_3(CO)_3$ (isomer II) (2.62, 2.66, and 2.71 Å),[47] $Rh_3(C_5H_5)_3(H)(C_5H_5)$ (2.72 Å),[42] $Rh_2(C_5H_5)_2(CO)_3$ Å),[35] $Rh_6(CO)_{16}$ (2.78 Å),[34] $Rh_4(CO)_{12}$ (2.73 Å),[48] and $[Rh_{12}(CO)_{30}{}^{2-}]$ (2.80 Å).[49]

The Rh(I)–Rh(III) electron-pair bond is presumed to have an important influence on the chemistry of $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$. This metal–metal interaction no doubt localizes the electron density of the Rh(I) along the z direction on the side of the square-planar ligand plane toward the interior of the tetranuclear rhodium cluster. Such a localization would reduce the negative charge in the z direction on the exterior side of the Rh(I) basal plane and thereby would make the Rh(I) susceptible to coordination with a Lewis base such as triphenylphosphine. In support of this hypothesis the reaction of $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ with $P(C_6H_5)_3$[6] gives as a first product a bis-triphenylphosphine adduct with the $P(C_6H_5)_3$ presumably coordinated with the Rh(I).[50] Without any Rh(I)–Rh(III) bond the Rh(I) would be much less likely to add another electron-donating ligand.

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