Crystal and Molecular Structure of Bis(triphenylphosphine)tetrakis(dimethylglyoximato)dirhodium. The Length of a Rhodium(II)-to-Rhodium(II) Single Bond[1,2]

K. G. Caulton[3] and F. A. Cotton*

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: The crystal structure of bis(triphenylphosphine)tetrakis(dimethylglyoximato)dirhodium monohydrate mono-1-propanolate, $Rh_2(C_4H_7N_2O_2)_4[(C_6H_5)_3P)]_2 \cdot H_2O \cdot C_3H_7OH$, was determined using 3307 statistically significant reflections within a sphere in reciprocal space bounded by $2\theta = 40°$. The unit cell is monoclinic with the dimensions $a = 18.695$ (6), $b = 13.417$ (5), $c = 22.817$ (7) Å, $\beta = 98.534$ (9)°, and systematic absences uniquely indicate the space group to be $P2_1/c$. The signs of enough reflections to solve the structure were determined by the symbolic addition method and the structure was then refined by the full-matrix least-squares technique to final residuals of $R_1 = 0.085$ and $R_2 = 0.068$. Rhodium and phosphorus atoms were allowed anisotropic temperature parameters, while all other atoms (except H) were restricted to isotropic ones. Hydrogen atoms were omitted and the six phenyl groups were treated as rigid bodies. The dinuclear molecule, which constitutes the crystallographic asymmetric unit, consists of two equivalent halves, $(C_6H_5)_3PRh(C_4H_7N_2O_2)_2$, linked by a Rh–Rh bond of length 2.936 (2) Å. The P–Rh–Rh–P chain is practically linear and the two $Rh(C_4H_7N_2O_2)_2$ groups whose mean planes lie perpendicular to the P–Rh–Rh–P axis have an essentially eclipsed rotational relationship. If the phenyl groups are neglected, the remaining, central part of the molecule has virtual D_{2d} symmetry. Other average principal bond lengths (Å) are: Rh–P, 2.438 (4); Rh–N, 1.99 ± 0.02; N–O, 1.33 ± 0.02. O···H–O distances are 2.54, 2.57, 2.66, and 2.72. It is shown that the Rh–Rh bond must be essentially a single bond, whence it follows that the observed length of the Rh–Rh bond sets an upper limit on the Rh^{II} covalent radius. Arguments are then presented to show that the much shorter Rh–Rh distance (2.386 Å) in the dinuclear acetate indicates multiple bonding in that compound.

In order to obtain information on the length of a single bond between rhodium atoms in the formal oxidation state II, we undertook a crystallographic study of the compound $[(C_6H_5)_3P(DMG)_2Rh]_2$ (DMG represents the monoanion of dimethylglyoxime, $C_4H_7N_2O_2^-$), which seemed likely, on the basis of an early report,[4] to contain such a bond. In this paper we present a detailed account of that investigation and a discussion of the results.

Experimental Section

Collection and Reduction of the Data. Bis(triphenylphosphine)tetrakis(dimethylglyoximato)dirhodium was prepared[4] by reducing $ClRh(DMG)_2P(C_6H_5)_3$ with a tenfold excess of $NaBH_4$ in a 9:1 mixture of methanol and water.

Anal. Calcd for $(RhC_{26}H_{29}N_4O_4P)_2$: C, 52.4; H, 4.88; mol wt, 1190. Found: C, 51.9; H, 5.0; mol wt (methanol), 1005.

The red crystals produced by the reaction contain methanol, which is lost rapidly in the air, with resultant fracturing of the crystals. Recrystallization from 9:1 1-propanol-water gave crystals suitable for crystallographic study; the composition of these crystals, which was subsequently revealed by the structure determination, is $Rh_2(C_4H_7N_2O_2)_4[P(C_6H_5)_3]_2 \cdot H_2O \cdot C_3H_7OH$.

Precession photographs (*h0l*, *h1l*, *h2l*, *0kl*, *1kl*, *2kl*) using Cu Kα radiation indicated Laue symmetry $2/m$. The observed systematic absences *h0l*, $l \neq 2n$, *0k0*, $k \neq 2n$, uniquely determine the space group as $P2_1/c$. A diamond-shaped plate of approximate dimensions 0.17 × 0.14 × 0.05 mm was mounted on a General Electric XRD-6 automated diffractometer in a general orientation. Unit cell dimensions were determined by least-squares refinement of the angular settings of 28 reflections (Mo Kα, λ 0.71070, 24°). These are $a = 18.695$ (6), $b = 13.417$ (5), $c = 22.817$ (7) Å, $\beta = 98.534$ (9)°. The observed density, measured by flotation in aqueous $ZnBr_2$ solution, is 1.54 ± 0.04 g cm^{-3}, while that calculated for four solvated (*vide infra*) formula units is 1.49 g cm^{-3}.

Intensities were measured by a scintillation counter using Zr-filtered Mo Kα radiation with a takeoff angle of 3°. The pulse-height discriminator was set to accept 90% of the Mo Kα peak. Scans were of the θ–2θ type with a scan rate of 2°/min. The scan in 2θ ranged from 0.7° below the Kα_1 peak to 0.7° above the Kα_2 peak for each reflection. Backgrounds were estimated by counting for 20 sec at each end of the scan range.

The intensities (I) of 5271 unique reflections over a range of 2θ from 0 to 40° were measured. Of these, 3307 were judged to be statistically significant on the basis of $I > 0$ and $I \geq 2\sigma(I)$.

Three standard reflections, distributed over a substantial range of θ, were each measured a total of 124 times during the data collection. There was no evidence for crystal decomposition. The measured intensities were corrected for Lorentz and polarization effects. Standard deviations of the derived structure factors were calculated according to Doedens and Ibers,[5] using an instrumental "uncertainty factor" of 2.6%. Absorption corrections were neglected ($\mu = 6.93$ cm^{-1}).

Solution and Refinement. Atomic scattering factors were those of Cromer and Waber.[6] All were corrected for the real and imaginary part of anomalous dispersion.[7]

The structure was determined using direct methods.[8] The first E map showed clearly all atoms except the methyl carbon atoms of the chelate rings and the solvent molecules. Least-squares refinement, treating the phenyl rings as rigid bodies, was followed by the calculation of a difference Fourier map which yielded the methyl carbon atom positions. Two cycles of least-squares refinement resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.106$ and $R_2 = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2} = 0.100$. Residual electron dens-

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[1] Supported in part by the U. S. Atomic Energy Commission; funds to purchase the automated diffractometer used were provided by the National Science Foundation.

[2] A preliminary report has appeared: K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 6517 (1969).

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

[7] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[8] J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).

Table I. Final Positional and Thermal Parameters[a]

Atom	x	y	z	B,[b] Å^2
$\mathrm{Rh_1}$	0.2297 (8)	0.1056 (0)	−0.2889 (6)	2.59
$\mathrm{Rh_2}$	0.2318 (8)	−0.0490 (1)	−0.1976 (6)	2.80
$\mathrm{P_1}$	0.2309 (5)	0.2284 (6)	−0.3670 (0)	2.95
$\mathrm{P_2}$	0.2419 (5)	−0.1743 (6)	−0.1189 (1)	3.23
$\mathrm{O_{1a}}$	0.1382 (1)	0.2225 (1)	−0.2270 (5)	4.84 (29)
$\mathrm{N_{1a}}$	0.1368 (5)	0.1559 (0)	−0.2689 (5)	4.23 (34)
$\mathrm{C_{1a}}$	0.0779 (3)	0.1175 (3)	−0.3004 (7)	3.79 (40)
$\mathrm{C_{3a}}$	0.0027 (2)	0.1546 (8)	−0.2877 (3)	8.04 (63)
$\mathrm{C_{2a}}$	0.0908 (2)	0.0483 (7)	−0.3416 (2)	4.77 (44)
$\mathrm{C_{4a}}$	0.0338 (9)	−0.0064 (9)	−0.3878 (7)	8.73 (68)
$\mathrm{N_{2a}}$	0.1585 (4)	0.0268 (9)	−0.3417 (9)	3.54 (32)
$\mathrm{O_{2a}}$	0.1788 (2)	−0.0409 (3)	−0.3813 (2)	5.02 (29)
$\mathrm{O_{1b}}$	0.2795 (3)	0.2566 (0)	−0.2003 (5)	5.12 (30)
$\mathrm{N_{1b}}$	0.3043 (1)	0.1841 (6)	−0.2343 (5)	4.33 (35)
$\mathrm{C_{1b}}$	0.3696 (8)	0.1631 (2)	−0.2407 (8)	5.33 (49)
$\mathrm{C_{3b}}$	0.4287 (6)	0.2280 (2)	−0.2009 (0)	8.74 (68)
$\mathrm{C_{2b}}$	0.3808 (8)	0.0930 (6)	−0.2789 (2)	4.15 (43)
$\mathrm{C_{4b}}$	0.4596 (3)	0.0669 (2)	−0.2890 (3)	6.93 (57)
$\mathrm{N_{2b}}$	0.3208 (5)	0.0537 (5)	−0.3081 (3)	4.10 (33)
$\mathrm{O_{2b}}$	0.3238 (4)	−0.0160 (2)	−0.3498 (5)	5.23 (31)
$\mathrm{O_{1c}}$	0.0999 (1)	−0.1328 (6)	−0.2576 (3)	7.70 (40)
$\mathrm{N_{1c}}$	0.1734 (4)	−0.1408 (5)	−0.2568 (3)	5.96 (42)
$\mathrm{C_{1c}}$	0.2188 (9)	−0.1975 (5)	−0.2849 (8)	7.39 (62)
$\mathrm{C_{3c}}$	0.1613 (0)	−0.2741 (7)	−0.3296 (7)	14.37 (106)
$\mathrm{C_{2c}}$	0.2861 (7)	−0.1863 (8)	−0.2725 (0)	6.13 (54)
$\mathrm{C_{4c}}$	0.3443 (4)	−0.2534 (5)	−0.2927 (1)	12.87 (98)
$\mathrm{N_{2c}}$	0.3066 (6)	−0.1197 (0)	−0.2335 (9)	4.86 (37)
$\mathrm{O_{2c}}$	0.3745 (5)	−0.1039 (6)	−0.2135 (8)	8.15 (40)
$\mathrm{O_{1d}}$	0.0886 (5)	0.0077 (2)	−0.1829 (6)	8.03 (41)
$\mathrm{N_{1d}}$	0.1562 (0)	0.0282 (1)	−0.1635 (3)	5.25 (39)
$\mathrm{C_{1d}}$	0.1812 (5)	0.0875 (1)	−0.1225 (2)	6.70 (59)
$\mathrm{C_{3d}}$	0.1233 (5)	0.1552 (6)	−0.0911 (2)	13.31 (99)
$\mathrm{C_{2d}}$	0.2473 (9)	0.1003 (0)	−0.1138 (3)	7.16 (60)
$\mathrm{C_{4d}}$	0.2968 (6)	0.1773 (5)	−0.0625 (8)	13.39 (100)
$\mathrm{N_{2d}}$	0.2925 (3)	0.0454 (4)	−0.1415 (4)	6.45 (43)
$\mathrm{O_{2d}}$	0.3634 (1)	0.0366 (0)	−0.1407 (7)	8.76 (44)
$\mathrm{O_{h2}}$	−0.0539 (3)	−0.1182 (5)	−0.3049 (6)	18.19 (87)
$\mathrm{C_{pr3}}$	0.4647 (0)	0.1394 (8)	−0.5096 (2)	35.07 (237)
$\mathrm{C_{pr2}}$	0.5003 (3)	0.1357 (3)	−0.5589 (8)	46.86 (604)
$\mathrm{C_{pr1}}$	0.5983 (7)	0.1312 (2)	−0.5465 (7)	20.64 (166)
$\mathrm{O_{pr}}$	0.5752 (2)	0.2390 (2)	−0.5649 (1)	22.56 (185)
$\mathrm{C_1}$	0.1683 (6)	−0.2087 (2)	−0.0788 (4)	2.95 (36)
$\mathrm{C_2}$	0.1018 (2)	−0.1593 (8)	−0.0863 (6)	3.98 (42)
$\mathrm{C_3}$	0.0488 (8)	−0.1863 (8)	−0.0521 (4)	5.34 (48)
$\mathrm{C_4}$	0.0623 (6)	−0.2628 (2)	−0.0104 (4)	5.96 (51)
$\mathrm{C_5}$	0.1288 (2)	−0.3122 (8)	−0.0028 (6)	5.14 (47)
$\mathrm{C_6}$	0.1818 (8)	−0.2852 (8)	−0.0370 (4)	4.84 (45)
$\mathrm{C_7}$	0.3119 (9)	−0.1374 (2)	−0.0577 (7)	3.77 (41)
$\mathrm{C_8}$	0.2888 (2)	−0.1043 (6)	−0.0055 (2)	4.69 (44)
$\mathrm{C_9}$	0.3393 (6)	−0.0708 (2)	0.0417 (2)	7.47 (61)
$\mathrm{C_{10}}$	0.4129 (9)	−0.0703 (2)	0.0368 (7)	5.52 (50)
$\mathrm{C_{11}}$	0.4360 (2)	−0.1035 (6)	−0.0154 (2)	5.83 (49)
$\mathrm{C_{12}}$	0.3855 (6)	−0.1370 (2)	−0.0626 (2)	4.14 (42)
$\mathrm{C_{13}}$	0.3183 (7)	0.2926 (9)	−0.3604 (9)	3.37 (39)
$\mathrm{C_{14}}$	0.3783 (5)	0.2561 (0)	−0.3835 (5)	5.09 (47)
$\mathrm{C_{15}}$	0.4446 (3)	0.3055 (2)	−0.3715 (3)	7.97 (64)
$\mathrm{C_{16}}$	0.4510 (7)	0.3914 (9)	−0.3365 (9)	6.12 (50)
$\mathrm{C_{17}}$	0.3909 (5)	0.4279 (0)	−0.3135 (5)	6.47 (55)
$\mathrm{C_{18}}$	0.3246 (3)	0.3785 (2)	−0.3254 (3)	5.21 (47)
$\mathrm{C_{19}}$	0.1700 (1)	0.3375 (1)	−0.3760 (2)	3.20 (38)
$\mathrm{C_{20}}$	0.1729 (4)	0.3962 (5)	−0.4262 (8)	4.76 (44)
$\mathrm{C_{21}}$	0.1311 (5)	0.4827 (6)	−0.4352 (7)	5.87 (51)
$\mathrm{C_{22}}$	0.0864 (1)	0.5104 (1)	−0.3940 (2)	4.79 (45)
$\mathrm{C_{23}}$	0.0834 (4)	0.4517 (5)	−0.3439 (8)	4.96 (44)
$\mathrm{C_{24}}$	0.1252 (5)	0.3652 (6)	−0.3349 (7)	4.11 (42)
$\mathrm{C_{25}}$	0.2097 (0)	0.1656 (9)	−0.4398 (8)	3.49 (39)
$\mathrm{C_{26}}$	0.1376 (9)	0.1675 (8)	−0.4667 (4)	5.24 (48)
$\mathrm{C_{27}}$	0.1165 (0)	0.1163 (8)	−0.5198 (8)	5.99 (50)
$\mathrm{C_{28}}$	0.1677 (0)	0.0632 (9)	−0.5460 (8)	5.60 (49)
$\mathrm{C_{29}}$	0.2399 (9)	0.0613 (8)	−0.5192 (4)	5.19 (47)
$\mathrm{C_{30}}$	0.2609 (0)	0.1125 (8)	−0.4661 (8)	4.78 (45)
$\mathrm{C_{31}}$	0.2649 (0)	−0.2964 (1)	−0.1452 (6)	2.69 (36)
$\mathrm{C_{32}}$	0.2083 (3)	−0.3488 (1)	−0.1786 (0)	4.30 (43)
$\mathrm{C_{33}}$	0.2200 (1)	−0.4449 (8)	−0.1986 (0)	6.89 (55)
$\mathrm{C_{34}}$	0.2883 (0)	−0.4888 (1)	−0.1853 (6)	7.20 (59)
$\mathrm{C_{35}}$	0.3448 (3)	−0.4364 (1)	−0.1519 (0)	7.50 (60)
$\mathrm{C_{36}}$	0.3331 (1)	−0.3402 (8)	−0.1319 (0)	5.37 (49)

Table I (*Continued*)

Atom	Anisotropic Thermal Parameters (Å^2 × 10^2)[c]					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$\mathrm{Rh_1}$	18.8 (5)	35.9 (10)	12.8 (3)	0.9 (6)	2.5 (3)	0.2 (5)
$\mathrm{Rh_2}$	21.9 (5)	36.4 (10)	13.9 (3)	3.8 (6)	3.0 (3)	0.1 (5)
$\mathrm{P_1}$	21.3 (18)	46.0 (37)	13.1 (12)	1.2 (20)	2.5 (11)	3.0 (17)
$\mathrm{P_2}$	27.8 (19)	40.4 (36)	14.9 (13)	0.4 (21)	4.7 (12)	4.4 (17)

[a] Numbers in parentheses are esd's in the last figure quoted for all tables. [b] Effective isotropic B's are given for the anisotropically refined atoms. [c] The form of the temperature-factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

ity in the vicinity of rhodium and phosphorus was indicative of anisotropic thermal motion. Refinement was continued varying only anisotropic thermal and positional parameters of these four atoms, thereby reducing R_1 to 0.089 and R_2 to 0.072. A new difference Fourier map showed an atom in a plausible position to be a water molecule hydrogen bonded to a dimethylglyoximate oxygen. In addition, a chain of four light atoms was evident, and this was assigned as a 1-propanol molecule. One terminal atom of this chain was assigned as an oxygen atom on the basis of a 2.9-Å contact with a dimethylglyoximate oxygen. Refinement of all parameters (using rigid-body phenyl rings) led to convergence with R_1 = 0.085 and R_2 = 0.068.

The weighting scheme $w(F_o) = \sigma^{-2}(|F_o|)$ was judged to be adequate by Cruickshank's criterion.[9] A comparison of the observed and calculated structure factors indicated that no correction for extinction was necessary. The final standard deviation of an observation of unit weight is 2.05. Calculation of the structure factors for the rejected reflections showed that less than 2.5% of the $|F_c|$ deviated from $|F_o|$ by more than 4σ.

A difference Fourier synthesis was computed using the final parameters.[10] With the exception of a peak in the vicinity of the rhodium atom, the largest peak, near a carbon atom ($\mathrm{C_{pr2}}$) of the propanol molecule, was equivalent to approximately 25% of a carbon atom. This observation, together with the large temperature factors of the propanol atoms, is suggestive of some disorder. Lack of interest in this molecule and cost considerations led us to abandon further attempts to improve the propanol refinement.

Computer Programs. Programs used in the structure determination include PICK2 (J. A. Ibers), for refining cell constants and generating angular settings for data collection; DIFDAR (A. S. Parkes), for data reduction; FORDAP (A. Zalkin), for Patterson and Fourier syntheses; FAME/MAGIC (R. Dewar and A. Stone), for calculating normalized structure factors (E's) and performing the symbolic addition; SFLS5 (C. T. Prewitt), for least-squares refinements based on minimization of the function $D = \Sigma w_F||F_o| - |F_c||^2$; MGEOM (J. S. Wood), for bond parameters and least-squares planes; and ORTEP (C. K. Johnson), for intermolecular contacts and diagrams. The program for rigid-body refinement of the phenyl groups has been described elsewhere.[11]

Results and Description of Structure

Fractional coordinates and thermal parameters are given in Table I. Tables II–V present data on bond lengths, bond angles, least-squares planes, and intermolecular contacts.

The structure of the dinuclear molecule, $[(C_6H_5)_3PRh(DMG)_2]_2$, is depicted in Figure 1. The molecule has no crystallographic symmetry and, because of the $(C_6H_5)_3P$ groups, it also lacks any overall virtual sym-

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(9) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965.

(10) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(11) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6675 (1968).

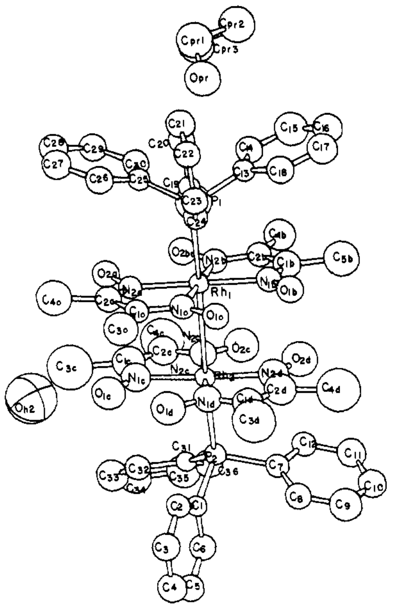

Figure 1. A view of the asymmetric unit, $Rh_2(C_4H_7N_2O_2)_4[(C_6H_5)_3P]_2 \cdot H_2O \cdot C_3H_7OH$, giving the atom numbering scheme.

metry. However, if the phenyl groups are neglected, the remainder of the molecule approximates closely to D_{2d} symmetry.

Table II. Bond Distances[a] (Å)

Atoms	Distance	Atoms	Distance
Rh_1-Rh_2	2.936 (2)	P_1-C_{13}	1.83 (1)
Rh_1-P_1	2.430 (5)	P_1-C_{19}	1.85 (1)
Rh_2-P_2	2.447 (5)	P_1-C_{25}	1.85 (2)
Rh_1-N_{1a}	1.98 (2)	P_2-C_1	1.82 (2)
Rh_1-N_{2a}	1.97 (1)	P_2-C_7	1.83 (2)
Rh_1-N_{1b}	2.02 (1)	P_2-C_{31}	1.82 (1)
Rh_1-N_{2b}	1.95 (2)	$O_{pr}-C_{pr1}$	1.54 (8)
Rh_2-N_{1c}	2.02 (2)	$C_{pr1}-C_{pr2}$	1.81 (12)
Rh_2-N_{2c}	1.97 (2)	$C_{pr2}-C_{pr3}$	1.39 (14)
Rh_2-N_{1d}	2.00 (2)	$O_{1a} \cdots O_{1b}$	2.66 (2)
Rh_2-N_{2d}	2.03 (2)	$O_{2a} \cdots O_{2b}$	2.72 (2)
		$O_{1c} \cdots O_{1d}$	2.57 (2)
		$O_{2c} \cdots O_{2d}$	2.54 (2)
		$O_{1c} \cdots O_{b2}$	2.92 (3)

	Distance			
	Ligand A	Ligand B	Ligand C	Ligand D
O_1-N_1	1.31 (2)	1.37 (2)	1.38 (2)	1.31 (2)
O_2-N_2	1.30 (2)	1.34 (2)	1.30 (2)	1.33 (3)
N_1-C_1	1.33 (2)	1.28 (3)	1.37 (3)	1.26 (3)
N_2-C_2	1.30 (2)	1.33 (2)	1.28 (3)	1.35 (3)
C_2-C_4	1.56 (3)	1.58 (3)	1.54 (4)	1.72 (4)
C_1-C_3	1.57 (3)	1.56 (3)	1.71 (4)	1.66 (4)
C_1-C_2	1.37 (3)	1.32 (3)	1.26 (4)	1.23 (4)

[a] Standard deviations in the last figure of each bond length are given in parentheses.

Some of the noteworthy structural features follow.

(1) Each of the DMG groups is planar.

(2) The two $Rh(DMG)_2$ groups are rotated 2.4° away from the perfectly staggered relationship which would be required for true D_{2d} symmetry.

(3) The two DMG groups on a given rhodium atom are hydrogen bonded across the O · · · O lines, as is typical, but they deviate slightly from coplanarity; the average of the two dihedral angles is 176.4°, with the bend being away from the $(C_6H_5)_3P$ groups. This bending is in the same sense as that found in $(C_6H_5)_3P(DMG)_2RhCl$[12] (162.9°) but is much less severe as might be expected. In the mononuclear complex such bending, which lessens repulsive interactions with the triphenylphosphine, encounters little opposition from the remaining ligand, Cl, whereas in the dinuclear molecule the two DMG groups on the other metal atom provide substantial opposition.

Table III. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
$P_1-Rh_1-Rh_2$	177.4 (1)	$Rh_1-N_{1a}-C_{1a}$	115.4 (12)
$Rh_1-Rh_2-P_2$	176.2 (1)	$Rh_1-N_{1b}-C_{1b}$	113.4 (13)
$P_1-Rh_1-N_{1a}$	92.4 (4)	$Rh_1-N_{2a}-C_{2a}$	116.8 (12)
$P_1-Rh_1-N_{2a}$	89.7 (4)	$Rh_1-N_{2b}-C_{2b}$	116.6 (13)
$P_1-Rh_1-N_{1b}$	91.0 (4)	$Rh_2-N_{1c}-C_{1c}$	109.9 (14)
$P_1-Rh_1-N_{2b}$	88.5 (5)	$Rh_2-N_{1d}-C_{1d}$	114.1 (15)
$P_2-Rh_2-N_{1c}$	92.7 (5)	$Rh_2-N_{2b}-C_{2c}$	118.0 (15)
$P_2-Rh_2-N_{2c}$	89.5 (5)	$Rh_2-N_{2d}-C_{2d}$	107.9 (15)
$P_2-Rh_2-N_{1d}$	93.0 (5)	$N_{1a}-Rh_1-N_{2a}$	77.7 (6)
$P_2-Rh_2-N_{2d}$	89.5 (5)	$N_{1b}-Rh_1-N_{2b}$	77.2 (6)
$Rh_2-Rh_1-N_{1a}$	88.6 (4)	$N_{1c}-Rh_2-N_{2c}$	77.0 (7)
$Rh_2-Rh_1-N_{2a}$	88.5 (4)	$N_{1d}-Rh_2-N_{2d}$	78.0 (7)
$Rh_2-Rh_1-N_{1b}$	90.8 (4)	$N_{1a}-Rh_1-N_{1b}$	103.2 (6)
$Rh_2-Rh_1-N_{2b}$	90.5 (5)	$N_{2a}-Rh_1-N_{2b}$	101.8 (6)
$Rh_1-Rh_2-N_{1c}$	91.2 (5)	$N_{1c}-Rh_2-N_{1d}$	103.4 (7)
$Rh_1-Rh_2-N_{2c}$	87.9 (5)	$N_{2c}-Rh_2-N_{2d}$	101.5 (7)
$Rh_1-Rh_2-N_{1d}$	89.5 (5)	$N_{1a}-Rh_1-N_{2b}$	179.0 (6)
$Rh_1-Rh_2-N_{2d}$	86.5 (5)	$N_{2a}-Rh_1-N_{1b}$	178.8 (11)
$Rh_1-N_{1a}-O_{1a}$	118.6 (10)	$N_{1c}-Rh_2-N_{2d}$	177.3 (9)
$Rh_1-N_{2a}-O_{2a}$	122.0 (10)	$N_{2c}-Rh_2-N_{1d}$	177.4 (7)
$Rh_1-N_{1b}-O_{1b}$	117.3 (10)	$Rh_1-P_1-C_{13}$	111.3 (4)
$Rh_1-N_{2b}-O_{2b}$	122.6 (10)	$Rh_1-P_1-C_{19}$	123.1 (5)
$Rh_2-N_{1c}-O_{1c}$	113.6 (12)	$Rh_1-P_1-C_{25}$	109.0 (5)
$Rh_2-N_{2c}-O_{2c}$	119.5 (12)	$Rh_2-P_2-C_1$	124.1 (5)
$Rh_2-N_{1d}-O_{1d}$	117.6 (12)	$Rh_2-P_2-C_7$	110.0 (5)
$Rh_2-N_{2d}-O_{2d}$	114.7 (13)	$Rh_2-P_2-C_{31}$	111.9 (5)
$C_{13}-P_1-C_{19}$	99.4 (6)	$C_7-P_2-C_{31}$	108.5 (7)
$C_{19}-P_1-C_{25}$	110.9 (8)	$C_{31}-P_2-C_1$	99.8 (7)
$C_{25}-P_1-C_{13}$	102.4 (7)	$O_{pr}-C_{pr1}-C_{pr2}$	118 (7)
$C_1-P_2-C_7$	101.1 (9)	$C_{pr1}-C_{pr2}-C_{pr3}$	76 (5)

	Angle, deg			
	Ligand A	Ligand B	Ligand C	Ligand D
$O_1-N_1-C_1$	126 (1)	129 (1)	136 (2)	128 (2)
$O_2-N_2-C_2$	121 (1)	121 (1)	122 (2)	137 (2)
$N_1-C_1-C_2$	115 (2)	119 (2)	120 (2)	117 (2)
$N_2-C_2-C_1$	115 (2)	114 (2)	115 (2)	122 (2)
$N_1-C_1-C_3$	118 (2)	114 (2)	104 (2)	118 (2)
$N_2-C_2-C_4$	117 (2)	126 (2)	118 (2)	110 (2)
$C_3-C_1-C_2$	127 (2)	127 (2)	137 (2)	124 (2)
$C_4-C_2-C_1$	128 (2)	120 (2)	126 (2)	128 (2)

[a] Standard deviations in the last figure quoted for each angle are given in parentheses.

(4) The mean plane of $N_{1a}-N_{2a}-N_{1b}-N_{2b}$ lies 2.88 Å from the mean plane of $N_{1c}-N_{2c}-N_{1d}-N_{2d}$. This separation is thus 0.05 Å less than the Rh-Rh distance; one Rh atom lies 0.01 Å beyond the plane of its nitrogen ligands while the other lies 0.04 Å beyond the corresponding plane.

(5) The two preceding features suggest that the observed rotational conformation about the Rh-Rh axis is dictated by repulsion between DMG ligands on different rhodium atoms.

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(12) F. A. Cotton and J. G. Norman, Jr., *J. Amer. Chem. Soc.*, **93**, 80 (1971).

Table IV. Weighted Least-Squares Planes[a]

	Plane	A^b	B	C	D	Angle between planes, deg
1.	$N_{1a}N_{2a}N_{1b}N_{2b}$	−0.0950	−0.0723	0.7056	−6.0758	178.5
2.	$N_{1c}N_{2c}N_{1d}N_{1d}$	−0.0773	−0.6903	0.7194	−3.1754	
3.	Ligand A	−0.1403	−0.7212	0.6784	−6.0986	176.1
4.	Ligand B	−0.0909	−0.6934	0.7148	−6.1201	
5.	Ligand C	−0.0918	−0.6763	0.7309	−3.3132	176.7
6.	Ligand D	−0.0746	−0.7150	0.6951	−3.0951	
7.	$Rh_1Rh_2M_aM_b{}^d$	−0.2599	0.6999	0.6652	−4.7483	92.4
8.	$Rh_1Rh_2M_cM_d{}^d$	0.9686	0.0747	0.2369	0.9009	
9.	$N_{1a}C_{1a}C_{2a}N_{2a}$	−0.1432	−0.7123	0.6871	−0.1569	176.3
10.	$N_{1b}C_{1b}C_{2b}N_{2b}$	−0.0863	−0.6989	0.7100	−6.0368	
11.	$N_{1c}C_{1c}C_{2c}N_{2c}$	−0.0756	−0.6900	0.7199	−3.1695	177.3
12.	$N_{1d}C_{1d}C_{2d}N_{2d}$	−0.0636	−0.7224	0.6885	−0.0204	

Distances of Atoms from Planes,[c] Å

1. N_{1a}, 0.001; N_{2a}, −0.001; N_{1b}, −0.001; N_{2b}, 0.001; Rh_1, −0.013; Rh_2, 2.92; N_{1c}, 2.93; N_{2c}, 2.87; N_{1d}, 2.88; N_{2d}, 2.83
2. N_{1c}, 0.002; N_{2c}, −0.003; N_{1d}, −0.003; N_{2d}, 0.003; Rh_2, 0.042; Rh_1, 2.89; N_{1a}, 2.89; N_{2a}, 2.93; N_{1b}, 2.83; N_{2b}, 2.86
3. O_{1a}, −0.004; N_{1a}, −0.018; C_{1a}, 0.011; C_{3a}, 0.049; C_{2a}, −0.005; C_{4a}, −0.057; N_{2a}, 0.024; O_{2a}, 0.000; Rh_1, −0.090
4. O_{1b}, −0.030; N_{1b}, 0.044; C_{1b}, 0.024; C_{3b}, −0.028; C_{2b}, 0.029; C_{4b}, −0.028; N_{2b}, 0.018; O_{2b}, −0.023; Rh_1, 0.006
5. O_{1c}, 0.026; N_{1c}, −0.014; C_{1c}, −0.051; C_{3c}, −0.006; C_{2c}, −0.060; C_{4c}, 0.111; N_{2c}, −0.045; O_{2c}, 0.031; Rh_2, 0.045
6. O_{1d}, −0.010; N_{1d}, 0.006; C_{1d}, 0.055; C_{3d}, −0.014; C_{2d}, −0.022; C_{4d}, −0.014; N_{2d}, 0.001; O_{2d}, 0.000; Rh_2, 0.100

[a] Atoms weighted by the inverse of their standard deviations. The orthogonal coordinate system (x, y, z) corresponds to the crystal axes a, b, c^*. [b] The equation of a plane is $Ax + By + Cz = D$. [c] Average esd's in atom positions are (Å): Rh, 0.0014; P, 0.0047; O, 0.014; N, 0.017; C, 0.025; C (methyl), 0.032. [d] M_a, M_b, M_c, and M_d are the midpoints of bonds C_{1a}–C_{2a}, C_{1b}–C_{2b}, C_{1c}–C_{2c}, and C_{1d}–C_{2d}, respectively.

Table V. Intermolecular Contacts

Atom A	Atom B	Vector from molecule containing A to molecule containing B	Distance, Å
O_{pr}	O_{2b}	$(1 - x, -y, -1 - z)$	2.91 (6)
O_{1a}	O_{h2}	$(-x, y + {}^1/_2, -{}^1/_2 - z)$	2.82 (3)

(6) The slight deviations of the Rh-Rh-P angles from 180° appear to be due to both intramolecular and intermolecular contacts between phenyl carbon atoms and DMG oxygen and nitrogen atoms.

(7) The water and propanol molecules are held in the crystal partly by hydrogen bonds to DMG oxygen atoms. The water molecule forms H bonds to O_{1c} of one molecule and O_{1a} of another, while the propanol molecules are H bonded to O_{2b} atoms. The variation in $O \cdots O$ distances mentioned above is at least partially correlated with this H bonding of the molecules of solvation since the shortest $O \cdots O$ distance is between those atoms which form no H bonds to H_2O or C_3H_7OH.

Discussion

The simplest and most obvious way to formulate the electronic structure of the molecule is to consider each rhodium atom to be octahedrally coordinated by the five conventional donor atoms (4N and P) and the other rhodium atom. In this way, after allowing the necessary orbitals and electrons for σ bonding, there remain three $d\pi$ orbitals and three electron pairs to occupy them. It is a natural, inherent part of this view (this is the same picture used for species such as $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $[Co_2(NCCH_3)_{10}]^{4+}$, which are isoelectronic and generally considered to have single bonds between the metal atoms) that the rhodium atoms are united by one pair of electrons. One could, purely formally, consider one rhodium atom as Rh^{III} with the other being Rh^{I} functioning as a two-electron donor; a resonance hybrid of the two equivalent representations of this type would then describe the equivalent, formally divalent rhodium atoms. While this approach is doubtless a strained and artificial one, it has the virtue of emphasizing the close relationship of the rhodium atoms in this dinuclear molecule with that in the mononuclear molecule $(C_6H_5)_3P(DMG)_2RhCl$, which *formally* appears to differ by containing Rh^{III}.

In a previous paper[12] the structures of $[(Ph_3P)(DMG)_2Rh]_2$ and $(Ph_3P)(DMG)_2RhCl$ were closely compared and it was concluded that the covalent radius for Rh^{II} is >1.4 Å, and most likely about 1.45 Å. Thus the length of an essentially unstrained Rh^{II}–Rh^{II} bond ought to be about 2.90 Å, with a rather firm lower limit of 2.80 Å.

It is interesting to compare this estimate of the length of a Rh^{II}–Rh^{II} single bond with the Rh-Rh distance actually found[13] in $Rh_2(O_2CCH_3)_4(H_2O)_2$, 2.386 Å, and indeed one of the main reasons for undertaking the studies of $[(Ph_3P)(DMG)_2Rh]_2$ and $(Ph_3P)(DMG)_2RhCl$ was to provide the basis for this and similar comparisons. Taken at face value, this comparison would seem unambiguously to require the conclusion that in the acetate the Rh-Rh bond is considerably more than single.

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[13] F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Amer. Chem. Soc.*, **92**, 2926 (1970).

This conclusion can be rationalized in a satisfying way if the bonding in $[(Ph_3P)(DMG)_2Rh]_2$ is reconsidered from a point of view which emphasizes its relationship to that of the dinuclear acetate.

In order to facilitate the intended comparison it is helpful to classify orbitals in both cases in terms of the D_{4h} symmetry of the acetate. Since the same degeneracies exist in D_{2d} and D_{4h} symmetries this is a tolerable approximation for the DMG compound. As discussed in detail elsewhere,[14] after allowance for four σ bonds from each metal atom to the approximately square set of ligands around it (the carboxylate oxygen atoms in the acetate, the DMG nitrogen atoms in $[(Ph_3P)(DMG)_2Rh]_2$) there remain on each metal atom five orbitals, two of which (d_{z^2}, p_z) are σ, two of which (d_{xz}, d_{yz}) are π, and one of which (d_{xy}) is δ with respect to the axis of true or approximate fourfold symmetry. The internuclear overlaps of these ten orbitals then lead to ten two-center MO's of which one σ, two π, and one δ MO will be of bonding character and, in the present cases, occupied by electron pairs. It is also very likely that there will be one rather strongly antibonding σ MO. It is with respect to the relative energies of the remaining five MO's and the distribution of the remaining electrons (three pairs for $Rh^{II}{}_2$) among them that differences of opinion may arise, and with regard to the case of $Rh_2(O_2CCH_3)_4(H_2O)_2$ have arisen.[14–16] To recapitulate, the MO's of interest, in order of increasing energies, are shown in (1) below.

The two orbitals $\sigma(a_{1g}{}^{(2)})$ and $\sigma(a_{2u}{}^{(1)})$ are particularly subject to variation in their position relative to the others in the middle group because (a) they can range in

$$\underset{\text{Rh–Rh bonding}}{\sigma(a_{1g}{}^{(1)}),\ \pi(e_u),\ \delta(b_{2g})} <$$

$$\underset{\text{Rh–Rh antibonding}}{\delta^*(b_{1u}),\ \pi^*(e_g),\ \sigma(a_{1g}{}^{(2)}),\ \sigma(a_{2u}{}^{(1)})} < \underset{\text{Rh–Rh antibonding}}{\sigma^*(a_{2u}{}^{(2)})} \quad (1)$$

character all the way from nonbonding when end groups are absent to strongly antibonding when end groups are strongly coordinated, and (b) they interact with the other σ orbitals, $\sigma(a_{1g}{}^{(1)})$ and $\sigma^*(a_{2u}{}^{(2)})$, so as to be split apart, lying in the order $\sigma(a_{2u}{}^{(1)}) < \sigma(a_{1g}{}^{(2)})$.

In the case of $[(Ph_3P)(DMG)_2Rh]_2$, where the end-group interactions are strong (Rh–P = 2.44 Å, as compared with the sum of radii, 1.45 (Rh) + 1.10 (P) = 2.55), we expect the $\sigma(a_{1g}{}^{(2)})$ and $\sigma(a_{2u}{}^{(1)})$ orbitals to be at quite high energies. Thus the three electron pairs still to be accommodated must occupy the $\delta^*(b_{1u})$ and $\pi^*(e_g)$ orbitals. In this way the bonding effect of the electrons in the $\delta(b_{2g})$ and $\pi(e_u)$ orbitals is approximately nullified and we are left with a net single σ bond between the rhodium atoms, as in the simple treatment of the electronic structure with which this discussion was begun.

In $Rh_2(O_2CCH_3)_4(H_2O)_2$, on the other hand, the axial interactions appear to be weak ($Rh-OH_2$ distance $\sim$ 0.27 Å longer than the Rh–O (acetate) distances). It is therefore plausible that the order of energies within the middle set or orbitals might be

$$\delta^*(b_{1u}) < \sigma(a_{2u}{}^{(1)}) < \sigma(a_{1g}{}^{(2)}) < \pi^*(e_g)$$

with electrons occupying all but the $\pi^*(e_g)$ orbitals. Thus, the Rh–Rh bond order would be nominally three due to the electron pairs in the $\sigma(a_{1g}{}^{(1)})$ and $\pi(e_u)$ orbitals, and the short Rh–Rh distance finds a natural explanation.

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(14) M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).

(15) L. Dubicki and R. L. Martin, *ibid.*, **9**, 673 (1970).

(16) Dubicki and Martin[15] have explicitly suggested that certain metal–ligand σ^* orbitals may lie low enough to be in the same energy region as the M–M nonbonding and antibonding orbitals. However, their energy level diagram shows these as being even lower than the $Rh-OH_2$ σ^* orbitals which scarcely seems credible, especially as it is now known that the $Rh-OH_2$ distances (2.31 Å) are far longer than the Rh–O (acetate) distances (2.04 Å). We shall assume here that only the five orbitals just mentioned in the text occur in this energy range.