Crystal and Molecular Structure of Chlorobis(dimethylglyoximato)triphenylphosphinerhodium(III)[1]

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Abstract: The crystal and molecular structure of chlorobis(dimethylglyoximato)triphenylphosphinerhodium(III), $Rh(C_4H_7N_2O_2)_2[P(C_6H_5)_3]Cl$, has been determined from the intensities of 5658 unique reflections collected with a counter diffractometer. The compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 9.826 (4), b = 10.896 (5), c = 25.125 (9) Å and β = 98.814 (8)°; ρ_{obsd} = 1.56 (5), ρ_{calcd} = 1.58 g/cm^3 for Z = 4. The structure, excluding hydrogen atoms, was solved by Patterson and Fourier syntheses and refined by full-matrix least-squares methods to a conventional R = 0.071 and weighted R = 0.055. The Rh–Cl and Rh–P distances are 2.381 (1) and 2.327 (1), Å, respectively; other average bond lengths include Rh–N = 1.992, C–N = 1.297, and N–O = 1.337 Å. The average O · · · O contact between dimethylglyoxime (DMG) rings is 2.663 Å. The Rh–Cl distance is used to derive a single-bond covalent radius for formal Rh(III) of 1.39 Å; on this basis the Rh(II)–Rh(II) bonds in $Rh_2(DMG)_4(PPh_3)_2$ (2.943 (2) Å) and $Rh_2(OAc)_4(H_2O)_2$ (2.386 (3) Å) are formulated as single and multiple, respectively.

The relation of bond length to bond multiplicity is a question of some interest for compounds containing direct metal–metal bonds, particularly since formal bond orders ranging from less than one (*e.g.*, in $Nb_6Cl_{12}^{2+}$) to as high as four (*e.g.*, in $Re_2Cl_8^{2-}$ and $Mo_2(OAc)_4$)[3] may be derived from qualitative molecular orbital (MO) considerations for such species. A collection of accurate metal–metal bond lengths for systems of idealized D_{4h} or D_{4d} symmetry is now available from X-ray studies,[3–5] and the observed distance trends are in general accord with the MO-based qualitative concept that, within a given structural type and transition-metal row, the bonds should weaken as the number of valence electrons of the metal increases past the d^4 configuration. However, a more quantitative correlation of bond orders with bond lengths is often complicated by lack of reliable values for metallic single-bond covalent radii in the systems under study, and hence lack of a precise idea of how long a metal–metal *single* bond should be. An example occurs in the carboxylate-bridged dimers of the formula $M_2(O_2CR)_4L_2$, where M = Cr, Mo, Re, Ru, Rh, Cu and L = H_2O, PPh_3, py, etc., whose general structure is shown in Figure 1. For a given M, the qualitative MO picture predicts a bond order ranging from n if the axial ligands L are very weakly donating to $n - 2$ if they form strong covalent bonds to the metal. A judgment of which M–L bonds are weak and which are strong is obviously somewhat subjective; in particular, for the case of $Rh_2(OAc)_4(H_2O)_2$ [n = 3, Rh–Rh = 2.386 (3), Rh–OH_2 = 2.308 (3) Å],[5] we have formulated the Rh–Rh bond as multiple,[3–5] while others have concluded that it is no more than single.[6] Our formulation is supported, we believe, by comparison of the acetate structure to that of the related $Rh_2(DMG)_4(PPh_3)_2$ [DMG = monoanion of dimethylglyoxime] shown in Figure 2. Here the principal distances are: Rh–Rh = 2.934 (2), Rh–P = 2.438 Å (average).[4] The Rh–P bond is certainly quite strong and the Rh–Rh bond, while necessarily somewhat elongated by repulsion between the two parallel DMG pairs, should have a multiplicity of one. In the course of preparing the DMG dimer, crystals of $Rh(DMG)_2(PPh_3)Cl$, the monomeric analog of the dimer with –Cl replacing the second –$Rh(DMG)_2(PPh_3)$ unit, were also obtained. Since the single-bond covalent radius of –Cl is well defined, it seemed worthwhile to determine the structure of this compound—in particular, the Rh–Cl distance—in order to derive a value for the single-bond covalent radius of rhodium which would be applicable to the closely related dimeric systems containing DMG and acetate. This paper reports the results of that structural determination. The synthesis of the compound has been reported previously.[7,8] It has attracted some recent interest as a starting material for the synthesis of "rhodoximes," analogs of the cobalt-containing model compounds for Vitamin B_{12}.[9]

Experimental Section

Collection and Reduction of X-Ray Data. Large, well-formed orange crystals of chlorobis(dimethylglyoximato)triphenylphosphinerhodium(III), $Rh(C_4H_7N_2O_2)_2[P(C_6H_5)_3]Cl$, were obtained from K. G. Caulton; they were prepared by a literature method.[7] Oscillation and Weissenberg photographs ($h0l$, $h1l$, $0kl$) on two crystals using Cu Kα radiation showed monoclinic symmetry with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, which uniquely identifies the space group as $P2_1/c$ (C_{2h}^5, No. 14). A prismatic crystal of approximate dimensions 0.16 × 0.16 × 0.36 mm was mounted on a General Electric XRD-6 automated diffractometer so that the b axis (coincident with the long axis of the crystal) was about 0.9° out of alignment with the φ axis. This was done to reduce the effects of multiple reflection.[10] Unit cell dimensions were determined using Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å) by least-

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[2] National Science Foundation Predoctoral Fellow.

[3] F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969), and references therein.

[4] K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 6517 (1969).

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

[6] L. Dubicki and R. L. Martin, *Inorg. Chem.*, **9**, 673 (1970).

[7] S. A. Shchepinov, E. N. Salnikova, and M. L. Khidekel, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2057 (1967).

[8] P. Powell, *J. Chem. Soc. A*, 2418 (1969).

[9] J. H. Weber and G. N. Schrauzer, *J. Amer. Chem. Soc.*, **92**, 726 (1970).

[10] W. A. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

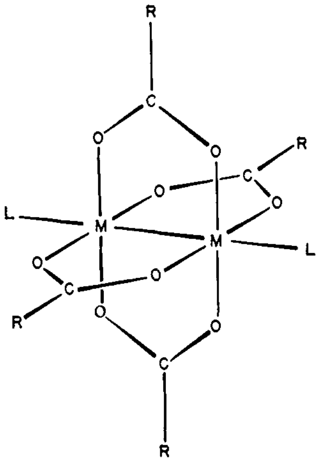

Figure 1. The general structure adopted by the compounds of formula $M_2(O_2CR)_4L_2$; M = Cr, Mo, Re, Ru, Rh, Cu.

squares refinement based on the accurately measured angular settings of 35 reflections; they are a = 9.826 (4), b = 10.896 (5), c = 25.125 (9) Å and β = 98.814 (8)°. These values lead to ρ_{calcd} = 1.58 g/cm^3 for Z = 4, ρ_{obsd} = 1.56 (5) g/cm^3 (flotation, CCl_4–heptane). With Z = 4 there is no crystallographic symmetry imposed on the molecule.

Intensities were measured by a scintillation counter using Zr-filtered Mo K$\bar{\alpha}$ radiation with a takeoff angle of 2°. The pulse-height discriminator was set to receive 95% of the Mo K$\bar{\alpha}$ peak. Scans were of the θ–2θ type with a scan rate of 2°/min. Angular widths of the scans varied as a function of the separation between α_1 and α_2 and included the region 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 of 6107 unique reflections within the range 2θ = 0–55° were collected. Of these, 449 were rejected because $I = P - B_1 - B_2 < 0$, where P = peak count and B_1 and B_2 = scaled background counts at the ends of the scan range. Inspection of the remaining 5658 reflections showed that, in the interval 2θ = 50–55°, more than 60% of the data still had $I \geq 3\sigma_I$ where $\sigma_I = (P + B_1 + B_2)^{1/2}$; therefore, no weak reflections were rejected on statistical grounds.

Three reflections ($5,0,\overline{18}$; $1,0,\overline{20}$; and $2,1,\overline{14}$) were remeasured at regular intervals throughout data collection as a check on crystal and instrument stability. A slight decrease in intensity with time, linear and uniform over the three reflections within the limits imposed by counting statistics and an assumed 1% machine error, was observed; the average intensity drop was 5.0%. A correction factor was applied to restore the intensities to their values at the beginning of data collection. The alignment of the crystal was carefully checked following data collection and found not to have changed within experimental error since the beginning of the process. The most probable cause of the decrease is therefore slight crystal decomposition, although this was not evident on visual inspection of the crystal following data collection.

The corrected intensities were used to calculate structure factor amplitudes $|F_o| = (I/Lp)^{1/2}$, where Lp = Lorentz–polarization factor, and their estimated standard deviations $\sigma_F = (4ILp)^{-1/2} \cdot [\sigma_I + (0.01I)^2]^{1/2}$. No correction for absorption was made; μ = 8.19 cm^{-1} for Mo K$\bar{\alpha}$ radiation and for the crystal mounted along b the maximum intensity variation due to absorption is therefore about 5.6% of the intensity through the shortest possible path.

Solution and Refinement. Atomic scattering factors used were those of Cromer and Waber.[11] All were corrected for the real and imaginary part of anomalous dispersion using the values for $\Delta f'$ and $\Delta f''$ given by Cromer.[12]

The positions of the rhodium, chlorine, and phosphorus atoms were located from a three-dimensional map of the Patterson function. Two cycles of least-squares refinement on these positions gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.356 and $R_2 = \Sigma w_F||F_o| - |F_c||^2/\Sigma w_F|F_o|^2$ = 0.411, where the weights were $w_F = \sigma_F^{-2}$. A difference Fourier synthesis was then computed, and from it the positions of the remaining 34 nonhydrogen atoms were determined. Three more cycles of refinement gave R_1 = 0.078 and R_2 = 0.065.

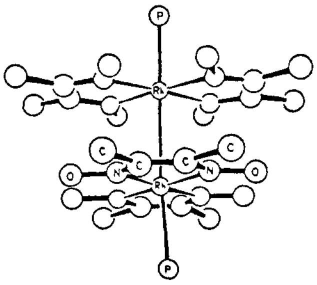

Figure 2. The structure of $Rh_2(DMG)_4[P(C_6H_5)_3]_2$. The phenyl groups are omitted for clarity.

An empirical weighting scheme $\sigma = \sigma_F \exp[3.382 - 5.263(\lambda^{-1} \sin \theta) + 1.916(\lambda^{-1} \sin \theta)^2]$ was introduced at this point to remove an observed ($\lambda^{-1} \sin \theta$) dependence in the quantity $w_F||F_o| - |F_c||^2$, in accordance with Cruickshank's criterion.[13] Anisotropic thermal parameters were introduced for the rhodium, chlorine, and phosphorus atoms, and two more cycles of refinement were carried out. The final R_1 and R_2 were 0.071 and 0.055, respectively; the decrease in both upon introduction of anisotropic thermal vibration parameters was found to be very significant at the 0.5% level using Hamilton's criterion.[14] Inspection of the final correlation matrix showed no significant correlation between any two parameters on different atoms. The esd of an observation of unit weight was 1.03, and the quantity $w_F||F_o| - |F_c||^2$ was now nearly independent of both $|F_o|$ and $\lambda^{-1} \sin \theta$; thus, the weighting scheme is satisfactory and an extinction correction was deemed unnecessary.

A difference Fourier synthesis was computed using the final parameters. The largest peak, in the vicinity of the rhodium atom, has a density of 1.34 electrons/Å^3. Several smaller peaks were found in chemically reasonable positions for hydrogen atoms, but no attempt was made to include them in the structure solution. Refinement was halted at this point since it was felt that the information desired from the structure did not justify the expense of treating any more than the three heavy atoms anisotropically, or of locating hydrogen atoms. However, the data appear to be of sufficient quality and quantity to warrant such treatment if there is interest in the information thereby to be gained.

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 synthesis; SFIX (local version of C. T. Prewitt's SFLS-5), for least-squares refinements based on minimization of the function $D = w_F||F_o| - |F_c||^2$; MGEOM (J. S. Wood), for bond parameters and least-square planes; and ORTEP (C. K. Johnson) for intermolecular contacts and diagrams.

Results and Description of Structure

A table of the final values of $|F_c|$ and $|F_o|$ scaled to $|F_c|$ is available.[15] Fractional coordinates and thermal parameters are given in Table I. Tables II–V present data on bond lengths, bond angles, least-squares planes, and those intermolecular contacts less than the sum of van der Waals radii, respectively. Figure 3 shows the molecular structure and presents the atom numbering scheme; Figure 4 depicts the significant intermolecular contacts.

The overall molecular structure reveals no surprises, but some finer details are of interest. The $Rh(DMG)_2$ system is not strictly planar; rather, the two C_2N_2 chelate rings are tilted away from the phenyl groups so

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

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

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

(14) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

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Table I. Final Positional and Thermal Parameters[a]

Atom	x	y	z	B,[b] Å^2
Rh	0.29375 (4)	0.35407 (4)	0.33770 (1)	2.000 (5)
Cl	0.2434 (2)	0.5323 (1)	0.28343 (5)	3.44 (3)
P	0.3437 (1)	0.1836 (1)	0.39309 (4)	2.27 (2)
O_1	0.1715 (5)	0.2204 (4)	0.2409 (1)	3.70 (7)
O_2	0.0012 (5)	0.3023 (5)	0.3084 (1)	3.90 (7)
O_3	0.5809 (4)	0.4357 (4)	0.3598 (1)	3.48 (6)
O_4	0.4139 (4)	0.5148 (4)	0.4241 (1)	3.35 (6)
N_1	0.2891 (5)	0.2635 (4)	0.2679 (1)	2.64 (6)
N_2	0.0950 (5)	0.3549 (5)	0.3455 (1)	2.90 (6)
N_3	0.4871 (4)	0.3725 (4)	0.3251 (1)	2.65 (6)
N_4	0.2975 (5)	0.4636 (4)	0.4010 (1)	2.54 (6)
C_1	0.4012 (6)	0.2686 (5)	0.2467 (2)	2.71 (7)
C_2	0.0617 (6)	0.4251 (6)	0.3828 (2)	3.21 (8)
C_3	0.5182 (5)	0.3318 (5)	0.2799 (2)	2.80 (7)
C_4	0.1782 (6)	0.4852 (6)	0.4159 (2)	2.97 (8)
Me_1	0.4120 (7)	0.2204 (7)	0.1915 (2)	4.0 (1)
Me_2	−0.0847 (9)	0.4525 (9)	0.3870 (3)	5.1 (1)
Me_3	0.6549 (7)	0.3493 (8)	0.2623 (2)	4.0 (1)
Me_4	0.1631 (7)	0.5689 (7)	0.4621 (2)	4.0 (1)
C_{11}	0.5261 (5)	0.1503 (6)	0.4019 (2)	2.95 (7)
C_{12}	0.5794 (6)	0.1037 (6)	0.3573 (2)	3.41 (9)
C_{13}	0.7180 (8)	0.0872 (7)	0.3586 (2)	4.4 (1)
C_{14}	0.810 (1)	0.1164 (9)	0.4050 (3)	5.7 (2)
C_{15}	0.758 (1)	0.158 (1)	0.4499 (3)	5.9 (1)
C_{16}	0.6187 (8)	0.1752 (7)	0.4486 (2)	4.2 (1)
C_{21}	0.2904 (5)	0.2029 (5)	0.4593 (2)	2.62 (7)
C_{22}	0.3518 (6)	0.2901 (6)	0.4961 (2)	3.26 (8)
C_{23}	0.3070 (7)	0.3024 (6)	0.5460 (2)	3.60 (9)
C_{24}	0.1991 (7)	0.2334 (7)	0.5582 (2)	3.8 (1)
C_{25}	0.1345 (7)	0.1497 (7)	0.5214 (2)	3.83 (9)
C_{26}	0.1825 (6)	0.1333 (6)	0.4723 (2)	3.42 (9)
C_{31}	0.2671 (6)	0.0367 (5)	0.3711 (2)	2.68 (7)
C_{32}	0.1372 (7)	0.0315 (6)	0.3391 (2)	3.58 (9)
C_{33}	0.0749 (8)	−0.0826 (7)	0.3271 (2)	4.3 (1)
C_{34}	0.1384 (8)	−0.1896 (8)	0.3457 (2)	4.5 (1)
C_{35}	0.2674 (8)	−0.1851 (7)	0.3771 (2)	4.1 (1)
C_{36}	0.3304 (7)	−0.0721 (6)	0.3901 (2)	3.60 (9)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			Anisotropic thermal parameters, Å^2 × 10^2 [c]			
Rh	2.55 (2)	2.56 (2)	2.52 (1)	0.003 (28)	0.50 (1)	−0.27 (1)
Cl	5.38 (9)	3.40 (7)	4.37 (5)	0.70 (6)	1.02 (5)	0.76 (5)
P	3.19 (7)	2.63 (6)	2.79 (4)	−0.11 (5)	0.43 (4)	−0.18 (3)

[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 $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}\cdot klb^*c^*]$.

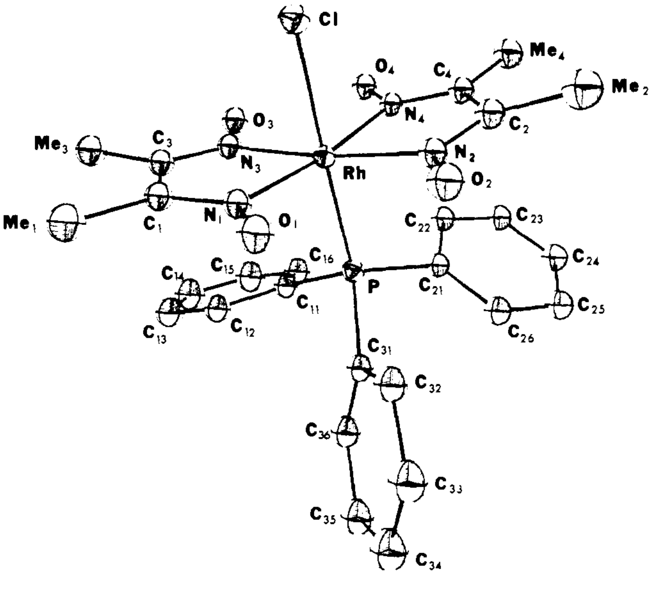

Figure 3. A perspective view of the molecular structure. The ellipsoids enclose 30% probability of thermal motion.

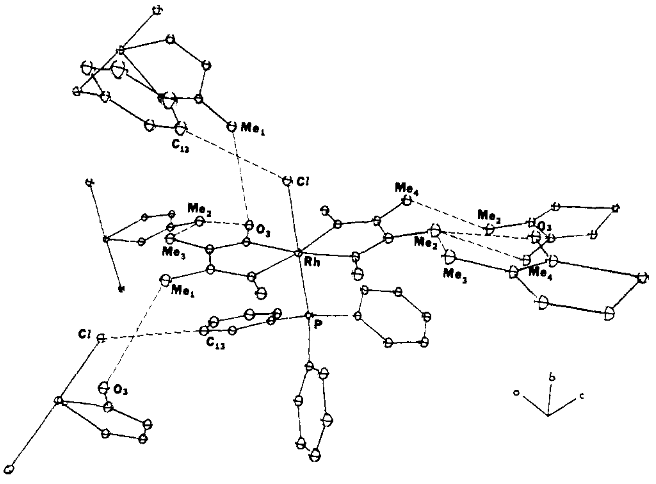

Figure 4. A perspective diagram showing one complete molecule and fragments of those with which it makes contacts less than the sum of van der Waals radii (including hydrogen atoms on methyl and phenyl carbon atoms). The contacts are indicated by dotted lines. The ellipsoids enclose 10% probability of thermal motion.

Table II. Bond Distances (Å)

Atoms	Distance	Atoms	Distance
Rh–Cl	2.381 (1)	P–C_{11}	1.809 (5)
Rh–P	2.327 (1)	P–C_{21}	1.830 (4)
Rh–N_1	2.007 (4)	P–C_{31}	1.818 (6)
Rh–N_2	1.992 (4)	C_{11}–C_{12}	1.40 (1)
Rh–N_3	1.984 (4)	C_{12}–C_{13}	1.37 (1)
Rh–N_4	1.984 (4)	C_{13}–C_{14}	1.40 (1)
N_1–O_1	1.333 (6)	C_{14}–C_{15}	1.39 (1)
N_2–O_2	1.336 (6)	C_{15}–C_{16}	1.38 (1)
N_3–O_3	1.356 (6)	C_{16}–C_{11}	1.40 (1)
N_4–O_4	1.324 (6)	C_{21}–C_{22}	1.40 (1)
C_1–N_1	1.295 (7)	C_{22}–C_{23}	1.40 (1)
C_2–N_2	1.289 (7)	C_{23}–C_{24}	1.37 (1)
C_3–N_3	1.298 (6)	C_{24}–C_{25}	1.38 (1)
C_4–N_4	1.306 (7)	C_{25}–C_{26}	1.40 (1)
C_1–C_3	1.481 (7)	C_{26}–C_{21}	1.38 (1)
C_2–C_4	1.462 (8)	C_{31}–C_{32}	1.40 (1)
C_1–Me_1	1.502 (7)	C_{32}–C_{33}	1.40 (1)
C_2–Me_2	1.489 (9)	C_{33}–C_{34}	1.37 (1)
C_3–Me_3	1.489 (8)	C_{34}–C_{35}	1.39 (1)
C_4–Me_4	1.500 (8)	C_{35}–C_{36}	1.39 (1)
$O_1 \cdots O_2$	2.709 (6)	C_{36}–C_{31}	1.39 (1)
$O_3 \cdots O_4$	2.618 (6)		

Table III. Principal Bond Angles (deg)

Atoms	Angle	Atoms	Angle
Cl–Rh–P	178.25 (5)	C_{11}–P–C_{21}	109.1 (3)
Cl–Rh–N_1	85.7 (1)	C_{21}–P–C_{31}	102.4 (2)
Cl–Rh–N_2	86.1 (1)	C_{11}–P–C_{31}	102.5 (3)
Cl–Rh–N_3	86.9 (1)	P–C_{11}–C_{12}	117.3 (3)
Cl–Rh–N_4	86.8 (1)	P–C_{21}–C_{22}	121.7 (4)
N_1–Rh–N_2	101.4 (2)	P–C_{31}–C_{32}	120.5 (4)
N_2–Rh–N_4	79.4 (2)	C_{16}–C_{11}–C_{12}	117.8 (5)
N_3–Rh–N_4	99.6 (2)	C_{11}–C_{12}–C_{13}	121.4 (5)
N_1–Rh–N_3	78.7 (2)	C_{12}–C_{13}–C_{14}	120.3 (8)
Rh–N_1–O_1	121.3 (3)	C_{13}–C_{14}–C_{15}	118.8 (9)
Rh–N_2–O_2	120.8 (3)	C_{14}–C_{15}–C_{16}	120.8 (7)
Rh–N_3–O_3	121.4 (2)	C_{15}–C_{16}–C_{11}	120.8 (8)
Rh–N_4–O_4	120.9 (3)	C_{26}–C_{21}–C_{22}	119.0 (4)
Rh–N_1–C_1	115.5 (3)	C_{21}–C_{22}–C_{23}	119.7 (5)
Rh–N_2–C_2	115.8 (4)	C_{22}–C_{23}–C_{24}	120.5 (6)
Rh–N_2–C_3	117.7 (4)	C_{23}–C_{24}–C_{25}	120.3 (5)
Rh–N_4–C_4	115.5 (3)	C_{24}–C_{25}–C_{26}	119.5 (6)
Rh–P–C_{11}	110.3 (2)	C_{25}–C_{26}–C_{21}	120.9 (6)
Rh–P–C_{21}	112.8 (2)	C_{36}–C_{31}–C_{32}	118.9 (5)
Rh–P–C_{31}	118.8 (2)	C_{31}–C_{32}–C_{33}	119.3 (5)
N_1–C_1–C_3	115.1 (5)	C_{32}–C_{33}–C_{34}	121.4 (6)
N_3–C_3–C_1	112.6 (5)	C_{33}–C_{34}–C_{35}	119.6 (7)
N_2–C_2–C_4	114.5 (5)	C_{34}–C_{35}–C_{36}	119.9 (5)
N_4–C_4–C_2	114.5 (5)	C_{35}–C_{36}–C_{31}	120.9 (5)
Me_1–C_1–C_3	121.5 (5)		
Me_3–C_3–C_1	123.4 (4)		
Me_2–C_2–C_4	123.4 (6)		
Me_4–C_4–C_2	123.4 (5)		

that their normal vectors make an angle of 17.1° with each other. As a result, though the N_4 system is rigorously planar, the rhodium atom is displaced from the plane toward the phosphorus by 0.126 Å. The two phenyl groups (C_{11}–C_{16}, C_{21}–C_{26}) close to the chelate rings may deviate very slightly from planarity, but the deviations are barely significant. The other phenyl group and the chelate rings show no significant deviations from planarity. The several close intermolecular contacts undoubtedly also influence the exact molecular configuration. As mentioned earlier, the molecule has no imposed crystallographic symmetry; it also has no idealized point-group symmetry. It is thus not surprising that different bonds between a given atom pair X and Y differ slightly in length. However, the deviations are not large, and hence one is justified in speaking of average bond lengths such as Rh–N = 1.992, C–N = 1.297, N–O = 1.337, and C–Me = 1.495 Å. The O$\cdots$O contacts of 2.618 and 2.709 Å are normal for H-bonded DMG rings.

Discussion

The most important structural feature in $Rh(DMG)_2(PPh_3)Cl$ for the purpose of this discussion is the Rh–Cl bond length of 2.381 (1) Å. Taking the covalent radius of chlorine as 0.994 Å, half the bond distance in Cl_2,[16] the value derived for the covalent radius of rhodium in this system is 1.39 Å. The expected length of an undistorted Rh–Rh *single* bond is therefore about 2.78 Å. The Rh–Rh distance of 2.934 (2) Å in $Rh_2(DMG)_4(PPh_3)_2$ thus clearly indicates a single bond, somewhat elongated by repulsion between the DMG pairs. It should be recognized that not all of the 0.15-Å difference between the observed distance and the calculated single-bond value arises from ligand repulsion. A considerable amount may be attributed to the slightly higher positive charge—and hence smaller covalent radius—expected for rhodium in the monomer than in the dimer. Put another way, the monomer contains *formally* Rh(III), the dimer Rh(II). Fortunately, a semiquantitative measure of the magnitude of this effect is available from comparison of the Rh–P distances, 2.327 (1) Å in the monomer and 2.438 Å (average) in the dimer. The major contribution to this difference is presumably the difference in formal oxidation state of rhodium, since the environments of phosphorus in the two compounds are otherwise quite similar. The value of 2.78 Å for a Rh–Rh single bond derived in the formally Rh(III) system is therefore a *lower limit* to the value expected in formally Rh(II) systems; a distance about 0.1 Å greater is anticipated for the latter case in the absence of additional repulsive forces. In the light of these facts, we believe that the Rh–Rh distance of 2.386 (3) Å in $Rh_2(OAc)_4(H_2O)_2$ indicates the existence of a multiple bond, as previously proposed. The value is about 0.5 Å shorter than the approximately 2.9 Å expected for a Rh(II)–Rh(II) single bond in this system by the above considerations. The difference is large enough to suggest a bond order which is considerably greater.

There are two features distinguishing the acetate from the DMG dimer which might possibly affect the metal–metal distance, but we think that neither will have a major effect on it. First, the axial ligand in the DMG system (PPh_3) has appreciable π-accepting ability, whereas the water molecule in the acetate does not. Whether the effect of this π acceptance on the metal–metal π system would be to lengthen or to shorten the metal–metal bond, it could scarcely be expected to change the distance by more than perhaps 0.1 Å, which would alter none of the conclusions drawn above. Second, it might be argued that the bridging acetates constrain the metal–metal bond to a shorter length by comparison to the DMG system, where the bond is unsupported by bridging groups. However, the accumulation of structural data on these systems clearly indicates that, while the bridging carboxylates provide an ideal framework for metal–metal interaction, the metals are free to move within the framework according

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[16] L. E. Sutton, Ed., *Chem. Soc. Spec. Pub.*, No. **18**, 1 (1965).

Table IV. Weighted Least-Squares Planes[a]

Plane	Equation	Angles between planes, deg
1. $N_1N_2N_3N_4$	$0.1119x - 0.8226y + 0.5574z = 1.552$	10.0 (6)
2. $C_1N_1C_3N_3$	$0.2338x - 0.8669y + 0.4403z = 0.862$	7.1 (7)
3. $C_2N_2C_4N_4$	$0.0237x - 0.7771y + 0.6289z = 2.374$	17.1 (7)
4. C_{11}–C_{16}	$-0.1360x - 0.9359y + 0.3250z = 1.230$	
5. C_{21}–C_{26}	$0.5919x - 0.6986y + 0.4026z = 3.675$	
6. C_{31}–C_{36}	$-0.5686x + 0.0578y + 0.8206z = 6.906$	

Distances of Atoms from Planes,[b] Å

1. N_1, −0.004; N_2, 0.004; N_3, 0.003; N_4, −0.004; Rh, 0.1256; O_1, −0.108; O_2, −0.125; O_3, 0.006; O_4, −0.025; C_1, −0.210; C_2, −0.162; C_3, −0.204; C_4, −0.128
2. N_1, 0.001; N_3, −0.001; C_1, −0.002; C_3, 0.002; Me_1, 0.075; Me_3, −0.026; O_1, −0.133; O_3, −0.033; Rh, −0.144
3. N_2, 0.006; N_4, −0.005; C_2, −0.017; C_4, 0.016; Me_2, −0.217; Me_4, 0.021; O_2, −0.146; O_4, −0.053; Rh, −0.061
4. C_{11}, −0.012; C_{12}, 0.009; C_{13}, 0.003; C_{14}, −0.020; C_{15}, 0.008; C_{16}, 0.011
5. C_{21}, 0.006; C_{22}, −0.017; C_{23}, 0.014; C_{24}, 0.005; C_{25}, −0.017; C_{26}, 0.009
6. C_{31}, −0.002; C_{32}, −0.002; C_{33}, 0.003; C_{34}, 0.002; C_{35}, −0.007; C_{36}, 0.006.

[a] The orthogonal coordinates (*x,y,z*) are directed along the crystal axes *a*, *b*, and *c**, respectively, and are in ångströms. The weight given to each atom *i* in forming the planes is $w_i = [a\sigma_{xi}b\sigma_{yi}c\sigma_{zi}]^{-2/3}$. [b] Average esd's of atomic positions are (Å): Rh, 0.0004; N, 0.004; O, 0.004; C_1–C_4, 0.006; Me, 0.008; C_{11}–C_{16}, 0.008; C_{21}–C_{26}, 0.007; C_{31}–C_{36}, 0.007.

Table V. Intermolecular Contacts Less than van der Waals Radii

Atoms		
Molecule A	Molecule B	Distance, Å
Cl	C_{13}	3.695 (7)
O_3	Me_1	3.364 (8)
O_3	Me_2	3.258 (8)
Me_2	Me_3	3.89 (1)
Me_2	Me_4	3.99 (1)

to their specific bonding requirements. Thus distances from 2.11 Å $[Mo_2(OAc)_4]$[17] to 2.72 Å $[Cu_2(O_2CH)_4NCS^{2-}]$[18] have been observed. Moreover, in several cases where isoelectronic systems with and without bridging carboxylato groups can be compared, such a constraining effect is at best slight. Thus the Mo–Mo distances in $Mo_2(O_2CCH_3)_4$ and $Mo_2Cl_8{}^{4-}$ are 2.11 and 2.14 Å, respectively.[17,19] Again, the Re–Re distances in $Re_2(O_2CC_6H_5)_4Cl_2$ and $Re_2Cl_8{}^{2-}$ are 2.235 and 2.241 Å, respectively.[20,21] It therefore seems unlikely that the Rh–Rh distance in the acetate is shortened to any significant extent over a hypothetical case where no bridging carboxylates are present.

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(17) D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, **87**, 921 (1965).

(18) D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Commun.*, 629 (1969).

(19) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 346 (1970).

(20) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *ibid.*, **7**, 1570 (1968).

(21) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

Reactions of Coordinated Ligands. Synthesis of a New Dinitrogen Complex

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Abstract: The reactions of *trans*-$[RuCl(NO)(das)_2]Cl_2$ [das is *o*-phenylenebis(dimethylarsine)] with nitrogen bases have been studied and found to involve nucleophilic attack at the nitrosyl nitrogen atom. With hydrazine as the nucleophile, the product formed is *trans*-$[RuN_3Cl(das)_2]$. This azide complex undergoes a novel reaction with $NOPF_6$ to yield the stable dinitrogen complex *trans*-$[RuClN_2(das)_2][PF_6]$. In the presence of oxygen, *trans*-$[RuN_3Cl(das)_2]$ is photochemically converted to the nitro complex, *trans*-$[RuCl(NO_2)(das)_2]$, which may also be prepared by the reaction of *trans*-$[RuClNO(das)_2]Cl_2$ with aqueous NaOH. ^{15}N-substituted complexes have been prepared and their infrared spectra utilized to determine the course of these reactions. Proton nmr spectra show that the complexes have the trans configuration.

The coordinated nitrosyl ligand is known to be rather inert to displacement by electron-pair donors such as cyanide, hydroxide, carbon monoxide, tertiary phosphines, etc. This inertness to displacement is undoubtedly due in part to the strong bonds formed between the transition metal and the nitrosyl group.