TABLE VI

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (A)[a]

Atom	Minimum	Intermediate	Maximum
Re	0.206 (2)	0.251 (2)	0.263 (1)
Cl_1	0.217 (7)	0.294 (7)	0.336 (6)
Cl_2	0.254 (7)	0.267 (6)	0.310 (6)
P_1	0.215 (7)	0.241 (8)	0.291 (7)
P_2	0.208 (8)	0.224 (7)	0.254 (7)
P_3	0.207 (8)	0.249 (7)	0.270 (7)

[a] Figure 2 provides an indication of the directions of these principal axes of vibration.

group phenyl atoms seem reasonable; there is the general trend that vibration is least for the C_1 atoms attached to P and greatest for the C_4 atoms *trans* to C_1. Similarly, the α-carbon atoms of the ethyl groups are vibrating less than the β-carbon atoms. In short, it appears that this particular data set is free enough from systematic errors so that the information on thermal motions derived from it has some elements of truth.

The derived bond distances may be "corrected" for the effects of thermal motion under various assumptions.[29] Perhaps the most reasonable assumption to make in the present case is that the lighter atoms are riding on the Re atom. The corrections for thermal motion are then rather small. For example, the Re–N bond distance becomes 1.782 A. This small decrease (0.006 A) occurs because the amplitude of vibration of the N atom normal to the Re–N bond is less than that of Re. It is important to keep in mind that generally the errors of assumption in the thermal model exceed the precision with which the bond distances have been determined. Thus great care must be exercised in discussing apparent, small differences in bond distances, especially in those determinations where the thermal motions of the atoms are poorly defined owing to residual systematic errors in the data.

Acknowledgments.—We are indebted to Professor J. Chatt and Miss R. J. Paske for supplying the crystals and for useful discussions. We have also enjoyed useful discussions with our colleagues, especially with Professors F. Basolo and R. G. Pearson. Dr. T. C. Furnas, Jr., has been of considerable assistance to us in problems related to the Picker diffractometer. The support of the National Institutes of Health, GM-12985, is gratefully acknowledged.

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(29) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

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Studies of Metal–Nitrogen Multiple Bonds. II. The Crystal and Molecular Structure of Nitridodichlorobis(triphenylphosphine)rhenium(V), $ReNCl_2(P(C_6H_5)_3)_2$

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The crystal and molecular structure of nitridodichlorobis(triphenylphosphine)rhenium(V), $ReNCl_2(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques down to a final R factor of 4.8% on F. The material crystallizes in space group C_{2h}^6-I2/a of the monoclinic system, with four molecules in a cell of dimensions $a = 15.71$, $b = 9.53$, $c = 22.17$ A; $\beta = 103°\,26'$. The crystal structure is made up of well-separated monomeric molecular units. Twofold crystallographic symmetry is imposed on the molecule. The inner coordination about Re is distorted from both idealized five-coordinate geometries: the trigonal bipyramid and the tetragonal pyramid. Roughly the structure may be described as a distorted tetragonal pyramid, with N at the apex and with the P atoms moved out of the basal plane of the Cl atoms toward the Re. The Re–Cl, Re–P, and Re–N distances are 2.377 ± 0.002, 2.448 ± 0.002, and 1.603 ± 0.009 A. Although the Re–Cl and Re–N distances differ markedly from those found in the closely related six-coordinated Re(V) complex, $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$, the nonbonded interligand distances in the two compounds are very similar.

Introduction

This paper describes the crystal and molecular structure of nitridodichlorobis(triphenylphosphine)rhenium(V), $ReNCl_2(P(C_6H_5)_3)_2$. This study is part of a series on the structures of complexes containing metal–nitrogen multiple bonds and it was undertaken for two interrelated reasons. First, the compound may be thought of as derived from $ReNCl_2(PR_3)_3$, in which the Re is six-coordinated, by removal of one PR_3 ligand with no resultant change in the formal oxidation state of Re (Re(V)). It seemed to us to be of obvious interest to carry out accurate structure determinations on both the six- and five-coordinated complexes in order that useful information on the relations of six- and five-coordination might be obtained. The first paper in this series[1] described the structure of $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$. Second, five-coordinate transition metal complexes are of interest in themselves, since no consistent

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(1) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

set of rules exists that allows one to predict which, if either, idealized geometry (trigonal bipyramidal or tetragonal pyramidal) will obtain in a given case.[2,3] Obviously, reliable experimental information on five-coordination is needed before much advance can be made on the theoretical side.

Collection and Reduction of the Intensity Data

Crystals of $ReNCl_2(P(C_6H_5)_3)_2$ were prepared by Miss R. J. Paske in the manner described by Chatt, *et al.*,[4] and were kindly supplied by Professor J. Chatt. Optical and X-ray examination of the small, well-formed orange crystals confirmed the monoclinic symmetry and lattice constants reported by Chatt, *et al.*[4] The lattice constants and standard deviations obtained by a least-squares refinement of the setting angles of 13 reflections which had been carefully centered on a Picker four-circle automatic X-ray diffractometer are: $a = 15.712 \pm 0.005$, $b = 9.531 \pm 0.004$, $c = 22.168 \pm 0.009$ A; $\beta = 103° 26' \pm 1'$ (t 28°; λ(Cu Kα_1) 1.5405 A). The extinctions observed on Weissenberg and precession photographs were hkl absent for $h + k + l$ odd and $h0l$ absent for h odd. These extinctions, which are those previously reported,[4] are consistent with either of the space groups C_{2h}^6-I2/a or C_s^4-Ia. The density of 1.65 g/cm^3 calculated for four molecules in the unit cell agrees satisfactorily with the reported[4] density of 1.63 g/cm^3. Thus if the space group is the centrosymmetric one, I2/a, then twofold molecular symmetry is imposed; if the space group is the noncentrosymmetric one, Ia, then no crystallographic symmetry need be imposed on the molecule.

The experimental and computational procedures used in data collection and processing parallel those described previously,[1] and only the differences will be emphasized. No crystal could be found that was large enough to be ground into a suitable sphere. The crystal used for gathering intensity data was a small plate of approximate dimensions 0.13 × 0.11 × 0.05 mm. In preparation for an absorption correction of the intensity data, the selected crystal was carefully measured by means of a micrometer eyepiece and the eight crystal faces were identified with the aid of an optical goniometer. The crystal was attached to the end of a small glass fiber and was then mounted roughly along a^* on the Picker diffractometer. Since the crystal was not oriented about a symmetry direction, the effects of multiple reflections were minimized.[5] The cell parameters and orientation angles were determined from a least-squares refinement of observations on a series of centered reflections in the manner previously described.[1] The small size and low mosaicity of the crystal were indicated by an average half-width of 0.06° on ω scans through several strong reflections by the narrow-source, open-counter technique.[6]

For reasons indicated earlier[1] Cu Kα radiation was employed in the data collection. The diffracted beams were filtered through 1.0-mil Ni foil. The intensities were collected by the θ–2θ scan technique at a take-off angle of 0.8°. At this take-off angle the peak intensity of a typical reflection was about 75% of its maximum value as a function of take-off angle. A symmetric scan range of 1.4° in 2θ was found to be sufficient for all reflections. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The scan rate was 1.0°/min. A counter aperture 3.5 mm high by 5.0 mm wide was used, and the aperture was placed 21 cm from the crystal.

Intensity data were collected from all possible forms of this monoclinic crystal (hkl, $\bar{h}\bar{k}\bar{l}$, $h\bar{k}l$, and $\bar{h}k\bar{l}$) up to θ(Cu Kα_1) $\leq$ 54°. Past this point, very few intensities were above background under the conditions of data collection just described. A total of 7169 intensities were collected. The data were processed in the manner described earlier[1] with the following exceptions. After initial correction for background, and estimation of the standard deviation $\sigma(I)$ of the corrected intensity I from the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in a scan of time t_c, B_1 and B_2 are the background counts, each obtained in time t_b, and $I = CT - 0.5 \cdot (t_c/t_b)(B_1 + B_2)$, and $p = 0.03$, the intensities were corrected for Lorentz-polarization factors, and then for absorption. The absorption correction was carried out by numerical methods using our version of the program GONO9, originally written by W. C. Hamilton. With the use of a calculated absorption coefficient of 101.1 cm^{-1} the corresponding transmission factors ranged from 1.6 to 2.7. This again emphasizes that even with very small crystals (ours had a computed volume of 0.00049 mm^3 corresponding to a weight of 0.8 μg) absorption corrections can be very important, especially if one wishes to achieve high accuracy in the description of the structure.

The anomalous scattering of Cu Kα radiation by Re (and even by P and Cl) cannot be ignored at the level of precision with which intensity data can be obtained by counter methods. In the presence of such anomalous scattering, Friedel's law, which states that $F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l})$ (F being the structure amplitude), breaks down if the space group is not centrosymmetric. Thus before the possibly equivalent F^2 values can be averaged, it is necessary to know which space group, I2/a or Ia, is the correct one. It may not be commonly realized that, in principle, the point group can be determined from the manner in which Friedel's law breaks down. Table I details this for the monoclinic system. In our case we wish to distinguish point group m (Ia) from point group 2/m (I2/a), and the absorption-corrected data, now corresponding to F^2 values, were examined to see if there were systematic variations among possibly equivalent forms that would correspond to point group m; *i.e.*, $F^2(hkl) \neq F^2(\bar{h}k\bar{l})$.

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[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

[3] E. L. Muetterties and R. A. Schunn, *Quart Rev.* (London), **20**, 245 (1966).

[4] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1012 (1964).

[5] W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

[6] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

No systematic variations could be detected. This, together with our failure to observe a piezoelectric effect, suggested that the correct space group is the centrosymmetric one, I2/a. As a final check on this, a Patterson function was calculated from the inner reflections and it too provided support for I2/a. Consequently, the four forms were averaged together and standard deviations were assigned in the manner described earlier.[1] Of the 1966 independent F^2 values thus obtained, 170 were less than one standard deviation above background. The weighted R factor, R_2, on F^2 is defined as $R_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$. If it is assumed that $\sigma(F^2)$ is a measure of $|F_o^2 - F_c^2|$, then one may, prior to the solution of the structure, compute an R_2 value from the F^2 and $\sigma(F^2)$ values; in our case we calculate R_2 to be 4.0%. If the range estimates of standard deviations do not exceed the individual estimates[1] and if the effects of counting statistics on $\sigma(F^2)$ are negligible, then the predicted value of R_2 should be $100p$ (3.0% in our case). An initial estimate of R_2 serves the useful function of preventing overrefinement of the data; in principle, the final value of R_2, as computed from the agreement of F_o^2 with the F_c^2 values from the final structure, should not be less than the initial value.

TABLE I

POINT GROUP DETERMINATION FROM FAILURE OF FRIEDEL'S LAW (MONOCLINIC SYSTEM, *b* AXIS UNIQUE)

Point group	Relations among squares of structure amplitudes
2	$F^2(hkl) = F^2(\bar{h}k\bar{l})$; $F^2(h\bar{k}l) = F^2(\bar{h}\bar{k}\bar{l})$; $F^2(hkl) \neq F^2(h\bar{k}l)$
m	$F^2(hkl) = F^2(h\bar{k}l)$; $F^2(\bar{h}k\bar{l}) = F^2(\bar{h}\bar{k}\bar{l})$; $F^2(hkl) \neq F^2(\bar{h}k\bar{l})$
2/m	$F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l}) = F^2(h\bar{k}l) = F^2(\bar{h}k\bar{l})$

Solution and Refinement of the Structure

The coordinates of the rhenium and one other atom (later shown to be a chlorine) were found from a three-dimensional Patterson function,[7] and two successive difference Fourier syntheses, with intermediate least-squares refinements, yielded the coordinates of the remaining nonhydrogen atoms. The Re and N atoms occupy the special fourfold positions of I2/a: $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm ({}^1/_4, y, 0)$; the remaining atoms are in the general eightfold positions: $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z; {}^1/_2 - x, y, \bar{z})$. Calculation of structure factors based on these trial coordinates yielded discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 24.0 and 25.6%, respectively, where the weights w were taken as $4F^2/\sigma^2(F^2)$. In all calculations of F_c, the atomic scattering factors tabulated by Ibers[8] were used for P, Cl, C, N, and H, and those of Cromer and Waber[9] were used for Re. The effects of anomalous dispersion were included in F_c;[10] the values of f' and f'' for Re, Cl, and P were those given by Cromer.[11]

Initial refinements were carried out on F, rather than F^2. After three cycles of isotropic least-squares refinement the values of R_1 and R_2 were 5.4 and 5.7%. A difference Fourier computed at this point showed evidence of anisotropic motion of the heavier atoms, although the maximum peak height of 1.4 e⁻/A³ indicated that the degree of anisotropy was not great. Although the peaks due to hydrogen atoms by no means dominated the map, the calculated positions of the 15 phenyl hydrogen atoms all lay on or near positive peaks ranging in height from 0.5 to 0.8 e⁻/A³.

Least-squares refinements were continued with the phenyl rings treated as rigid groups, use being made of the group-refinement program NUGLS.[1] Comparison of the weighted R factor of 5.9% obtained after the initial group refinement employing isotropic thermal parameters with that of 5.7% obtained in the unrestricted refinement indicates[12] that the unrestricted refinement is better than the group refinement at the 0.5% significance level. This statistical test is based on the premise that there are only random errors in the data. Again[1] it seems to us more reasonable to conclude that there are residual systematic errors in the data that invalidate the statistical test, rather than to conclude that the phenyl rings are significantly distorted. In two further cycles of group least-squares refinement, anisotropic thermal parameters were assigned to the Re, Cl, and P atoms. In agreement with the modest degree of anisotropy deduced from the difference map, the R factors dropped only slightly to 5.2 and 5.8%. An additional cycle in which the hydrogen atoms (C–H = 1.08 A) were included as fixed atoms lowered the R factors to 4.8 and 4.9%.

For the reasons outlined in the previous paper,[1] a final cycle of least-squares refinement was based on F^2; that is, the function $\Sigma w(F_o^2 - F_c^2)^2$ was minimized, where the weights w were taken as $1/\sigma^2(F^2)$. In this final cycle the parameter shifts were small, with 12 parameters shifting by amounts greater than their standard deviations, the highest shift being 1.9σ. The final values of R_1 and R_2 (*based on* F^2) were 7.8 and 9.7%. These parameters (Table II) lead to a value of R_1 (based on F) of 4.8%. The estimated standard deviation of an observation of unit weight is 1.37, indicating that the standard deviations of the intensity data were underestimated only slightly. A difference map based on the final parameters contains no peaks higher than 1.4 e⁻/A³.

Comparison of the final values of F_o and F_c did not suggest that a correction for secondary extinction was needed.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement on F^2 are presented in Table II, along with the corresponding standard deviations in these parameters as derived from the inverse matrix. The corresponding positional parameters of the group carbon atoms are presented in Table III. The final values of $10F_o$ and $10F_c$ (in electrons) are given in Table IV.

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[7] In addition to our various local programs for the CDC 3400, the programs used in this work were local modifications of Zalkin's FORDAP Fourier program and of the Busing–Levy ORFFE error function program.

[8] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

[10] J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

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

[12] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

TABLE II

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $ReNCl_2(P(C_6H_5)_3)_2$

Atom	x	y	z	β_{11}[a] or B, A^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.25	0.26567 (5)[b]	0.0	0.002551 (26)	0.006471 (74)	0.001226 (14)	0.0	0.000361 (14)	0.0
Cl	0.14683 (15)	0.34962 (23)	0.05463 (10)	0.00360 (11)	0.01114 (30)	0.00176 (6)	0.00165 (16)	0.00069 (6)	−0.00014 (11)
P	0.36453 (14)	0.30334 (22)	0.09443 (10)	0.00273 (10)	0.00686 (27)	0.00143 (5)	−0.00026 (14)	0.00042 (6)	0.00026 (10)
N	0.25	0.09756 (96)	0.0	2.8 (2)					

Group	x_c[c]	y_c	z_c	δ	ϵ	η	B_1, A^2	B_2, A^2	B_3, A^2	B_4, A^2	B_5, A^2	B_6, A^2
Ring 1	0.3413 (3)	0.1361 (4)	0.2156 (2)	1.911 (4)	−0.306 (3)	−2.030 (4)	2.8 (2)	2.8 (2)	3.8 (2)	4.5 (2)	5.4 (3)	4.9 (2)
Ring 2	0.5546 (3)	0.1955 (4)	0.0845 (1)	−0.404 (3)	0.085 (4)	0.291 (4)	2.6 (2)	3.2 (2)	4.4 (2)	3.8 (2)	5.0 (2)	4.0 (2)
Ring 3	0.3745 (3)	0.6318 (4)	0.1278 (2)	2.316 (13)	1.274 (4)	−0.793 (13)	2.7 (2)	3.6 (2)	5.0 (2)	5.0 (2)	5.4 (3)	4.2 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] x_c, y_c, and z_c are the fractional coordinates of the ring centers. The angles δ, ϵ, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system have been defined in previous papers: S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). B_i is the isotropic thermal parameter of atom i in a given ring. The rings are numbered so that C_1 is attached to P; C_4 is *para* to C_1.

TABLE III

DERIVED PARAMETERS FOR GROUP CARBON ATOMS

		Ring 1	
C_1	0.3510 (4)[a]	0.2103 (6)	0.1636 (2)
C_2	0.2752 (3)	0.1330 (6)	0.1615 (2)
C_3	0.2655 (4)	0.0588 (6)	0.2136 (3)
C_4	0.3316 (5)	0.0619 (6)	0.2677 (2)
C_5	0.4073 (4)	0.1392 (7)	0.2697 (2)
C_6	0.4170 (3)	0.2134 (7)	0.2177 (3)
		Ring 2	
C_1	0.4735 (3)	0.2472 (6)	0.0891 (2)
C_2	0.5449 (4)	0.3371 (4)	0.0965 (3)
C_3	0.6260 (3)	0.2854 (6)	0.0920 (3)
C_4	0.6357 (3)	0.1438 (6)	0.0800 (3)
C_5	0.5643 (4)	0.0539 (4)	0.0726 (3)
C_6	0.4831 (3)	0.1056 (5)	0.0771 (3)
		Ring 3	
C_1	0.3722 (6)	0.4891 (5)	0.1144 (5)
C_2	0.3564 (4)	0.5354 (6)	0.1703 (3)
C_3	0.3586 (4)	0.6781 (6)	0.1837 (3)
C_4	0.3767 (6)	0.7745 (5)	0.1413 (5)
C_5	0.3926 (5)	0.7282 (6)	0.0854 (4)
C_6	0.3903 (4)	0.5855 (6)	0.0719 (3)

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analyses on inter-ring distances. Intra-ring distances, of course, are fixed (C–C = 1.392 A).

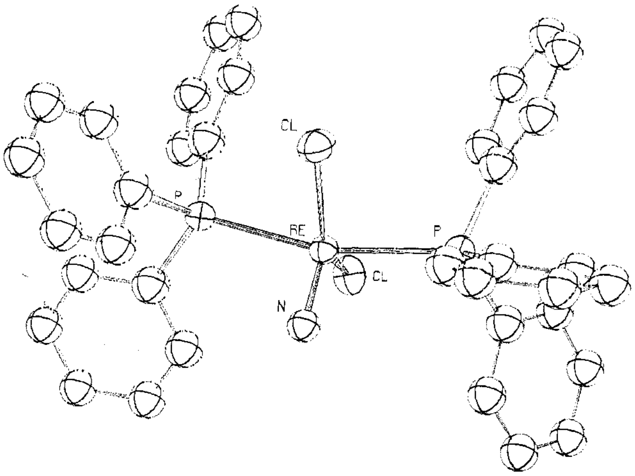

Figure 1.—A perspective drawing of the molecular structure of $ReNCl_2(P(C_6H_5)_3)_2$.

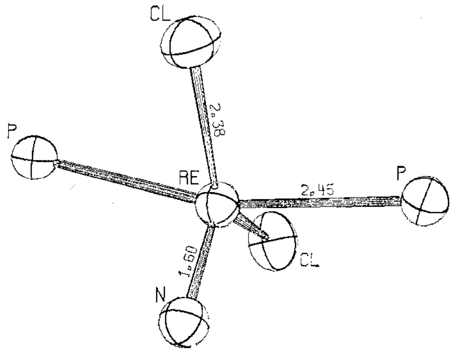

Figure 2.—A perspective drawing of the inner coordination sphere in $ReNCl_2(P(C_6H_5)_3)_2$.

Description of the Structure

The unit cell dimensions, symmetry operations, and parameters of Table II lead to a crystal structure made up of loosely packed monomeric molecular units. In Figure 1 the over-all molecular structure is displayed; in Figure 2 only the inner coordination about the Re atom is shown. Principal intramolecular distances and angles and their estimated standard deviations, as derived from the data of Table II and the correlation matrix, are given in Table V. Only the closest intermolecular approaches to Re and N are tabulated in Table V. The packing of the molecules is almost entirely dictated by intermolecular interactions of the bulky phenyl groups: the volume per triphenylphosphine group is 404 A^3, approximately 10% higher than in triphenylphosphine itself.[13] All intermolecular interactions appear to be normal.

The molecule itself, by virtue of the imposed crystallographic twofold axis, has symmetry C_2. This symmetry is consistent with either of the two idealized five-coordinate geometries: the trigonal bipyramid or the tetragonal pyramid. In the present case the molecule has an intermediate geometry, and it is a matter of taste whether one wishes to describe the coordination around Re as that of a distorted trigonal bipyramid or a distorted tetragonal pyramid. The distortions from trigonal-bipyramidal geometry are: the apical P atoms are displaced so that the P–Re–P angle, rather than being 180°, is 163°; the angles about Re in the basal plane, rather than being 120°, are 110, 110, and 140°.

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(13) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

TABLE IV: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR ReNCl$_2$(P(C$_6$H$_5$)$_3$)$_2$

H	L	OBS	CALC
***** K= 0 *****			
0	0		15515
0	2	3582	3504
0	4	631	552
0	6	922	798
0	8	590	490
0	10	2761	2583
0	12	3077	3041
0	14	1920	1856
0	16	783	761
0	18	1658	1556
0	20	1236	1285
0	22	1158	1245
2	0	2761	2815
2	2	265	231
2	-2	4094	3693
2	4	4716	4740
2	-4	1615	1443
2	6	5170	5041
2	-6	2795	2567
2	8	2576	2396
2	-8	2425	2321
2	10	2020	1860
2	-10	1149	1226
2	12	531	521
2	-12	2729	2616
2	14	734	651
2	-14	2510	2387
2	16	1163	1178
2	-16	1832	1736
2	18	1837	1811
2	-18	1175	1326
2	20	1071	1200
2	-20	1111	1121
2	-22	511	547
4	0	1491	1432
4	2	1552	1617
4	-2	2412	2094
4	4	4108	4261
4	-4	3001	2685
4	6	3992	3820
4	-6	3133	2986
4	8	2476	2486
4	-8	3455	3283
4	10	2192	2078
4	-10	2032	1979
4	12	895	852
4	-12	2052	2017
4	14	1286	1299
4	-14	2416	2386
4	16	1396	1324
4	-16	1463	1423
4	18	907	971
4	-18	875	888
4	20	634	652
4	-20	776	836
4	-22	442	512
6	0	1379	1455
6	2	2484	2680
6	-2	582	626
6	4	2195	2240
6	-4	3456	3124
6	6	1182	1243
6	-6	3670	3473
6	8	1831	1791
6	-8	3135	3091
6	10	1803	1701
6	-10	2388	2306
6	12	1945	1862
6	-12	574	587
6	14	1961	1939
6	-14	1491	1516
6	16	998	972
6	-16	1178	1245
6	18	585	720
6	-18	1155	1196
6	-20	996	991
6	-22	662	674
8	0	3637	3785
8	2	2159	2277
8	-2	2564	2631
8	4	409	418
8	-4	1519	1517
8	6	538	551
8	-6	2238	2105
8	8	1071	1028
8	-8	1638	1593
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12	-4	781	729
12	-6	843	850
12	-8	1019	1001
12	-10	951	959
13	-3	674	698
13	-5	833	857
13	-7	579	599
***** K= 7 *****			
0	1	793	748
0	3	709	804
0	5	406	567
0	7	735	761
0	9	1027	997
0	11	1329	1327
0	13	872	533
0	15	231	280
1	0	807	811
1	2	1015	1049
1	-2	786	798
1	4	1317	1307
1	-4	1079	1032
1	6	1158	1186
1	-6	1746	1677
1	8	555	571
1	-8	1257	[illegible]
1	10	837	862
1	-10	743	640
1	12	945	999
1	-12	769	755
1	14	787	801
1	-14	556	608
1	-16	740	763
2	1	793	827
2	-1	960	925
2	3	123	108
2	-3	1350	1274
2	5	179	159
2	-5	1330	1283
2	7	712	706
2	-7	913	840
2	9	1031	1038
2	-9	448	539
2	11	941	915
2	-11	561	593
2	13	628	715
2	-13	790	706
2	15	451	483
2	-15	321	287
3	0	1226	1163
3	2	1413	1433
3	-2	926	981
3	4	1173	1211
3	-4	599	569
3	6	676	637
3	-6	1225	1204
3	8	463	554
3	-8	1497	1454
3	10	767	761
3	-10	958	893
3	12	958	916
3	-12	729	680
3	14	927	870
3	-14	540	477
3	-16	516	477
4	1	738	790
4	-1	686	675
4	3	615	579
4	-3	385	894
4	5	1080	1091
4	-5	1264	1258
4	7	855	872
4	-7	1302	1299
4	9	108	185
4	-9	244	239
4	11	58	69
4	-11	67	48
4	13	415	462
4	-13	205	272
4	-15	620	576
5	0	1563	1579
5	2	1004	1026
5	-2	1746	1711
5	4	344	397
5	-4	938	698
5	6	470	473
5	-6	199	242
5	8	1069	1071
5	-8	752	654
5	10	1006	1046
5	-10	845	901
5	12	757	828
5	-12	1077	1026
5	-14	960	945
5	-16	982	955
6	1	850	894
6	-1	887	901
6	3	949	972
6	-3	647	703
6	5	996	1031
6	-5	269	189
6	7	670	735
6	-7	812	858
6	9	57	64
6	-9	355	283
6	11	449	465
6	-11	570	546
6	-13	514	555
6	-15	677	577
7	0	503	505
7	2	574	585
7	-2	704	735
7	4	1014	1009
7	-4	1197	1203
7	6	1323	1373
7	-6	918	889
7	8	932	960
7	-8	865	791
7	10	395	427
7	-10	755	741
7	-12	785	821
7	-14	882	835
8	1	846	823
8	-1	975	855
8	3	840	856
8	-3	414	400
8	5	454	559
8	-5	106	63
8	7	300	359
8	-7	327	331
8	9	550	533
8	-9	814	838
8	-11	942	888
8	-13	959	965
9	0	645	647
9	2	580	652
9	-2	623	648
9	4	707	748
9	-4	954	909
9	6	835	872
9	-6	1034	991
9	-8	723	750
9	-10	701	630
9	-12	766	800
10	1	333	264
10	-1	364	403
10	3	414	413
10	-3	492	514
10	5	435	419
10	-5	550	595
10	-7	667	640
10	-9	854	848
10	-11	672	619
11	0	645	651
11	2	765	766
11	-2	453	549
11	-4	462	521
11	-6	937	976
11	-8	1012	1010
***** K= 8 *****			
0	0	606	615
0	2	857	927
0	4	832	827
0	6	1032	963
0	8	771	741
0	10	346	354
0	12	472	497
1	1	506	448
1	-1	619	601
1	3	355	411
1	-3	500	593
1	5	726	662
1	-5	918	911
1	7	871	834
1	-7	1141	1103
1	9	811	809
1	-9	932	886
1	11	794	790
1	-11	775	725
1	13	576	589
1	-13	481	482
2	0	768	705
2	2	1053	1175
2	-2	533	604
2	4	907	932
2	-4	595	587
2	6	969	1005
2	-6	846	821
2	8	456	492
2	-8	872	889
2	10	332	310
2	-10	778	646
2	12	635	704
2	-12	499	473
3	1	677	649
3	-1	1255	1231
3	3	329	303
3	-3	1320	1272
3	5	407	413
3	-5	1032	1044
3	7	407	401
3	-7	405	459
3	9	644	709
3	-9	351	334
3	11	551	575
3	-11	400	423
3	-13	645	653
4	0	1119	1119
4	2	1125	1080
4	-2	610	599
4	4	724	730
4	-4	275	220
4	6	525	506
4	-6	591	575
4	8	406	452
4	-8	810	760
4	10	677	652
4	-10	1120	1068
4	-12	980	934
5	1	1002	1024
5	-1	947	897
5	3	955	959
5	-3	759	699
5	5	592	613
5	-5	644	551
5	7	427	417
5	-7	574	565
5	9	292	292
5	-9	311	431
5	-11	435	438
5	-13	502	422
6	0	694	738
6	2	171	134
6	-2	934	974
6	4	336	365
6	-4	959	916
6	6	727	743
6	-6	821	760
6	8	903	941
6	-8	615	588
6	-10	346	354
6	-12	900	869
7	1	763	781
7	-1	425	405
7	3	869	924
7	-3	284	273
7	5	578	904
7	-5	427	419
7	7	657	657
7	-7	713	677
7	-9	632	629
7	-11	589	553
8	0	603	535
8	2	451	448
8	-2	603	758
8	4	608	591
8	-4	705	767
8	-6	657	665
8	-8	795	826
8	-10	272	214
9	1	360	370
9	-1	457	468
9	-3	223	286
9	-5	405	442
9	-7	672	654
***** K= 9 *****			
0	1	663	575
0	3	791	791
0	5	563	547
0	7	607	644
0	9	900	867
1	0	525	530
1	2	829	809
1	-2	487	449
1	4	875	810
1	-4	615	651
1	6	669	726
1	-6	671	614
1	8	367	360
1	-8	451	448
1	-10	202	194
2	1	851	760
2	-1	762	716
2	3	521	521
2	-3	888	844
2	5	425	382
2	-5	939	893
2	7	659	651
2	-7	531	452
2	-9	771	768
3	0	663	678
3	2	922	920
3	-2	135	167
3	4	682	671
3	-4	72	66
3	6	552	561
3	-6	595	531
3	8	346	367
3	-8	746	676
3	-10	518	758
4	1	601	607
4	-1	592	701
4	3	644	636
4	-3	554	603
4	5	765	755
4	-5	1269	1184
4	-7	746	645
4	-9	448	418
5	0	764	752
5	2	309	292
5	-2	671	611
5	4	205	233
5	-4	237	226
5	-6	379	380
5	-8	537	475
6	1	789	751
6	-1	894	826
6	3	809	748
6	-3	429	434
6	-5	354	437
6	-7	261	450
7	0	392	412
7	-2	773	748
7	-4	706	760
***** K=10 *****			
0	0	451	459

TABLE V

SELECTED DISTANCES (A) AND ANGLES (DEGREES)

Intramolecular distance		Angle	
Re–Cl	2.377 (2)	Cl–Re–P	88.14 (7)
Re–P	2.448 (2)	Cl–Re–N	109.69 (6)
Re–N[a]	1.602 (9)	Cl–Re–Cl_1[d]	140.63 (11)
Cl–P	3.357 (3)	Cl–Re–P_1[d]	86.20 (7)
Cl–P_1	3.297 (3)		
Cl–N	3.283 (7)	P–Re–P_1	163.13 (10)
P–N	3.117 (6)	P–Re–N	98.44 (5)
P–R_1C_1[b]	1.826 (6)	R_1C_1–P–R_2C_1	101.9 (3)
P–R_2C_1	1.823 (6)	R_1C_1–P–R_3C_1	106.4 (3)
P–R_3C_1	1.822 (6)	R_2C_1–P–R_3C_1	106.9 (3)
Intermolecular distances			
Re–Re	≥ 9.04		
Re–P_1H_2	3.09[c]		
N–R_2H_4	2.80[c]		

[a] The Re–N distance corrected for thermal motion is 1.606 A for the riding model. Corrections to other distances are correspondingly small. For further comments on this problem see the remarks at the end of ref 1. [b] R_1C_1 refers to carbon atom 1 of phenyl ring 1. [c] Closest intermolecular distance to the first named atom. [d] The subscripts "1" on P and Cl refer to atoms related to those given in Table II by the twofold symmetry operation.

The distortion from a tetragonal pyramid results from the facts that the P and Cl atoms do not lie in the same plane and that the N–Re–P angle (98°) differs from the N–Re–Cl angle (110°).

The Re–P distance of 2.448 A compares favorably with those of 2.442, 2.469, and 2.490 found in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$[1] and with those of 2.45 and 2.48 A found in $ReOCl_3(P(C_2H_5)_2C_6H_5)_2$,[14] but all of these distances are somewhat long when compared with a variety of second- and third-row transition metal–phosphine distances found in other complexes. (See the discussion in ref 1 for specific examples.) On the other hand, the Re–Cl distance of 2.377 A found here is considerably shorter than those of 2.454 and 2.563 A found in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$[1] and is more in keeping with the usual M–Cl distance, for example in the $Re_2OCl_{10}^{4-}$ ion[15] (2.38 A).

The P–C distances and C–P–C angles are well within the range that has been observed in a number of complexes of triphenylphosphine. Again it is evident from Figure 1 that the dihedral angles between adjacent phenyl rings can vary greatly.

Cotton and Lippard[16] have derived a Re(V) radius of 1.38 A in the bromorhenates, with the use of Pauling's[17] value of 1.11 A for the Br radius. On this basis, again using Pauling's radii tables, they suggest that the Re–O single-bond length should be 2.04 A. They further suggest that the Re–O bond length of 1.86 A found in the $Re_2OCl_{10}^{4-}$ ion[15] should be a typical Re=O double-bond length. It turns out that these two values fit Pauling's empirical rule that $D(n) = D(1) - 0.6 \log n$, where $D(n)$ is the length of the bond of order n. On this basis one is tempted to suggest that the Re≡O triple-bond length should be 1.75 A, a value close to that found by Cotton and Lippard.[16] If we assume that the covalent radius for N is 0.04 A longer than for O[17] and if we neglect possible corrections for electronegativity differences, then the theoretical values of the Re–N bond lengths are: single, 2.08 A; double, 1.90 A; triple, 1.79 A. The last value is essentially what we observed in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$. The question then arises as to the possible factors which lead to the Re–N bond length of 1.60 A in the present five-coordinated compound $ReNCl_2(P(C_6H_5)_3)_2$. Clearly, one does not expect, again using the language of Pauling, a bond of order greater than 3 between Re and N. One possible suggestion is that the same nonbonded interactions can be achieved in the six-coordinate structure only at the expense of longer Re–ligand distances. In Table VI we give a comparison of the comparable nonbonded interligand distances in the two complexes. It seems to us that the agreement is remarkably good, despite the large variations in *bonded* Re–ligand distances. Thus we conclude that metal–ligand distances can be shorter in five-coordinate than in six-coordinate structures, and yet the nonbonded interligand distances can be the same. Unfortunately, we are unaware of any other examples, such as those presented here, where the structures of closely related five- and six-coordinate compounds with the metal in the same formal oxidation state are known to high accuracy. The obvious next step in this series of investigations is to examine closely related five- and six-coordinate structures containing the Re–N–C_6H_5 grouping; we anticipate that the Re–N distance will again be considerably longer in the six-coordinate than in the five-coordinate complex.

TABLE VI

INTERLIGAND DISTANCES IN $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$ AND $ReNCl_2(P(C_6H_5)_3)_2$

	Distance, A, in	
Interaction	$ReNCl_2(P(C_2H_5)_2C_6H_5)_3$	$ReNCl_2(P(C_6H_5)_3)_2$
N···Cl	3.26	3.29[a]
N···P	3.02, 3.11, 3.16	3.12
Cl_1···P	3.35, 3.35	3.36, 3.30
Cl_2···P[b]	3.55, 3.25, 3.58	...

[a] There are two of each such interactions in this compound. [b] Cl_2 is *trans* to N in the six-coordinate structure and has no direct counterpart in the five-coordinate structure.

Thermal Motions of the Atoms

In Table VII we list the mean-square amplitudes of vibration of those atoms which were refined anisotropically. The directions of vibration can be seen in Figure 2. The vibrations here are somewhat less than they are in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$,[1] and this is consistent

TABLE VII

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (A)[a]

Atom	Minimum	Intermediate	Maximum
Re	0.169 (1)	0.173 (1)	0.176 (1)
Cl	0.179 (4)	0.205 (3)	0.246 (3)
P	0.170 (4)	0.180 (3)	0.192 (3)

[a] Figure 2 provides an indication of the directions of these principal axes of vibration.

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[14] H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 4368 (1963).

[15] J. C. Morrow, *Acta Cryst.*, **15**, 851 (1962).

[16] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).

[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

with the difference in melting points (220° for the present compound *vs.* 153° for $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$[4]).

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Crystal Structure of Bis(*p*-toluidinium) Hexachlororhenate(IV)

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The structure of bis(*p*-toluidinium) hexachlororhenate(IV) has been determined. The space group is monoclinic $P2_1/c$ with four molecules per unit cell; the cell dimensions are $a = 7.01 \pm 0.02$, $b = 25.04 \pm 0.05$, $c = 11.54 \pm 0.02$ A; $\beta = 90.0 \pm 0.1°$. Octahedral $ReCl_6$ anions are packed with planar *p*-toluidinium cations such that the octahedra form layers alternated with organic groups, and the usual bond lengths and angles are maintained. The compound is apparently not magnetically dilute.

Introduction

The magnetic susceptibility of some simple Re(IV) salts, including K_2ReCl_6, Cs_2ReCl_6, and K_2ReF_6, has been reported by Figgis, Lewis, and Mabbs.[1] The interpretation of these measurements is complicated by the possibility of magnetic exchange. In an attempt to dilute the $ReCl_6$ ions with relatively large organic species and thereby reduce the exchange interaction, Figgis, *et al.*, also measured the susceptibility of bis(*p*-toluidinium) hexachlororhenate(IV) $[(TH)_2ReCl_6]$, bis(pyridinium) hexachlororhenate(IV), and bis(quinolinium) hexachlororhenate(IV). We have determined the crystal structure of $(TH)_2ReCl_6$ in order to observe the nature of this dilution and to provide structural data to facilitate the interpretation of the magnetic measurements.

Experimental Section

Bright yellow-green crystals of bis(*p*-toluidinium) hexachlororhenate $[(CH_3C_6H_4NH_3)_2ReCl_6]$ were prepared by combining 0.25 g of *p*-toluidinium hydrochloride with 0.25 g of potassium hexachlororhenate in 30 ml of concentrated HCl, heating to dissolve, and evaporating on a steam bath until crystals appeared. After standing overnight at room temperature the crystals were filtered on a sintered-glass funnel, washed twice with ethanol and twice with ether, and suction dried. K_2ReCl_6 was made by reduction of $KReO_4$ with H_2PO_3 in concentrated HCl.[2]

A single crystal approximately 0.5 × 0.05 × 0.005 mm was mounted on a glass fiber with the long dimension as the axis of rotation. Cell dimensions were obtained from rotation and Weissenberg photographs using Cu Kα radiation (λ 1.5418 A). Multiple-film equiinclination Weissenberg photographs were taken for layers $h = 0$–4, yielding 1812 independent nonzero reflections. The intensities were estimated by visual comparison with a calibrated film strip, corrected for spot size elongation and contraction,[3] and converted to structure factors in the usual way. Absorption corrections were not made. Interlayer scaling was done according to exposure time.

Unit Cell and Space Group

The crystals are monoclinic with $a = 7.01 \pm 0.02$, $b = 25.04 \pm 0.05$, $c = 11.54 \pm 0.02$ A; $\beta = 90.0 \pm 0.1°$. There are four formula weights per unit cell giving a calculated density of 2.02 g/cc. The density measured by flotation is 1.99 g/cc. The systematic absence of $h0l$ reflections when l is odd and of $0k0$ reflections when k is odd suggests $P2_1/c$ as the space group. The successful structure determination confirms this choice.

Determination of the Structure

A three-dimensional Patterson map yielded the rhenium and chlorine atom coordinates; four cycles of least-squares refinement[4] with these coordinates gave a value of 0.24 for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. An electron density map with signs based on rhenium and chlorine coordinates revealed the light-atom positions except for hydrogen which was ignored throughout the structure determination. Nitrogen atoms were distinguished from carbon atoms on chemical grounds only, as being closest to the hexachlororhenate octahedra. Seven cycles of full-matrix, least-squares refinement, using isotropic temperature factors for each atom, reduced R to 0.16. In these and subsequent least-squares calculations the function minimized was $\Sigma w(F_o - F_c)^2$ where the weights, w, were assigned according to Hughes.[5] Atomic scattering factors for neutral atoms were obtained from the listing of Ibers.[6] The layers were rescaled by making $\Sigma F_o = \Sigma F_c$. Introduction of anisotropic temperature factors in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ for rhenium and chlorine and removal of 14 intensities which either suffered from extinction or were

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(1) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 3138 (1961).

(2) G. W. Watt and R. J. Thompson, *Inorg. Syn.*, **7**, 190 (1963).

(3) K. Lonsdale, *Acta Cryst.*, **17**, 308 (1964).

(4) Fourier calculations were carried out with the FORDAP program of Dr. Allan Zalkin; least-squares calculations were done with the Gantzel–Sparks–Trueblood program.

(5) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(6) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 212.