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Studies of Metal-Nitrogen Multiple Bonds. I. The Crystal and Molecular Structure of Nitridodichlorotris(diethylphenylphosphine)rhenium(V), $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$

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The crystal and molecular structure of nitridodichlorotris(diethylphenylphosphine)rhenium(V), $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$, 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 5.1% on F . The material crystallizes in space group $\text{C}_{2h}^5\text{-P}2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a = 18.67$, $b = 11.51$, $c = 18.19$ Å; $\beta = 122^\circ 34'$. The individual molecular units are well separated. The inner coordination around Re is octahedral. If the three P atoms and one Cl atom are taken to define an equatorial plane, then N and the other Cl are above and below this plane, respectively. The octahedral configuration is somewhat distorted. Multiple bonding between the Re and N atoms is suggested by several features of the molecular structure: (1) the Re-N distance is 1.778 ± 0.011 Å; (2) there is some over-all lengthening of the equatorial distances (Re-Cl = 2.454 ± 0.004 Å; Re-P = 2.442 ± 0.004 , 2.469 ± 0.005 , 2.490 ± 0.005 Å); (3) the Re-Cl distance of 2.563 ± 0.004 Å *trans* to N is exceedingly long.

Introduction

Chatt and co-workers^{1,2} have recently described the preparation and characterization of a number of compounds which contain multiple bonds between nitrogen and rhenium. These compounds are of three types: $\text{ReX}_3(\text{NAr})(\text{PR}_3)_2$, $\text{ReNX}_2(\text{PR}_3)_3$, and $\text{ReNX}_2(\text{PR}_3)_2$ (X = halogen, Ar = aryl, R = alkyl or aryl). Of these, the latter two types are of particular interest, being new members of the small group of compounds which contain a nitrogen atom bonded only to a transition metal. These nitrido complexes are of structural interest for two reasons: first, there is no definitive information on metal-nitrogen multiple bonds; second, these compounds provide the opportunity to study the stereochemical relationships between very similar six- and five-coordinated structures, where the formal oxidation state of the metal remains the same [Re(V)]. It is our contention that through such studies really useful information is provided to the theoretical chemist whose task it is to understand the relative importance of those factors which affect the stereochemistry of transition metal complexes. A third reason that these compounds are of structural interest has arisen during the course of these studies. There have now been two reports of transition metal complexes containing molecular nitrogen.^{3,4} The metal-nitrogen bond distances obtained in the present studies, together with those known in such complexes as the amines of transition metals, should enable an estimate to be made of the degree of multiple bonding in metal-nitrogen systems, when a system suitable for structural study is discovered. For these reasons we also will extend our studies of metal-nitrogen multiple bonds to include the arylimido complexes of the type $\text{ReX}_3(\text{NAr})(\text{PR}_3)_2$.

Indeed, if one is to provide useful information on the interrelationships of these various compounds, then highly accurate structures are essential. Consider, for example, the related problem of multiple bonding between rhenium and oxygen. In three such studies [$\text{ReOCl}_3(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$,⁵ $((\text{C}_2\text{H}_5)_4\text{N})(\text{ReBr}_4\text{O}(\text{H}_2\text{O}))$,⁶ and $((\text{C}_6\text{H}_5)_4\text{As})(\text{ReBr}_4\text{O}(\text{CH}_3\text{CN}))$]⁷ the Re-O bond lengths vary between 1.60 and 1.73 Å. However, the estimated standard deviations on these bond lengths range from 0.04 to 0.06 Å. Thus, nothing meaningful can be said about the variations in the Re-O bond length from one compound to the next. This paper and the following one report structures in which the estimated standard deviation of the metal-nitrogen distance is 0.01 Å. The over-all quality of the determination is better, by perhaps a factor of 2, than we have achieved previously using film methods. These determinations presumably owe their high accuracy to several factors: (1) the use of scintillation counter data, (2) the multiple observation of each reflection through its equivalent forms, and (3) the careful handling of the absorption problem.

This paper is concerned with the structure of the compound $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$, nitridodichlorotris(diethylphenylphosphine)rhenium(V). The following paper discusses the structure of $\text{ReNCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ and the interrelationships between these two structures.

Collection and Reduction of the Intensity Data

Crystals of $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$ were prepared by Miss R. J. Paske and generously supplied by Professor J. Chatt. Optical and preliminary X-ray examination of the yellow, well-formed crystals confirmed the monoclinic symmetry reported by Chatt, *et al.*² The lattice constants, obtained by the least-squares procedure described below, are: $a = 18.669 \pm 0.004$, $b = 11.514$

(1) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).(2) J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *ibid.*, 1012 (1964).(3) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).(4) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).(5) H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 4368 (1963).(6) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965).(7) F. A. Cotton and S. J. Lippard, *ibid.*, **5**, 416 (1966).

± 0.002 , $c = 18.186 \pm 0.004$ Å; $\beta = 122^\circ 34' \pm 1'$ (t 28° , $\lambda(\text{Cu } K\alpha_1)$ 1.5405 Å). The cell reported by Chatt, *et al.*,² has the same b and c axes as this cell, but has an a axis defined in terms of our cell as $a + c/2$. Their cell is thus not a complete unit cell, but rather is half of a B-centered cell which has an a axis twice as long as their reported a . The systematic absences of $0k0$ for k odd and $h0l$ for l odd observed on a series of precession and Weissenberg photographs strongly suggest that the space group is C_{2h}^5 - $P2_1/c$. The calculated density of 1.55 g/cm³ for four molecules in the unit cell agrees well with the reported density² of 1.56 g/cm³. Thus, no crystallographic symmetry conditions need be imposed on the molecule.

Diffraction data were collected from a nearly spherical crystal of average diameter 0.20 mm. The crystal was mounted on a glass fiber about an axis normal to the (01 $\bar{1}$) planes, and in this orientation intensity data were collected on a Picker four-circle automatic X-ray diffractometer. The linear absorption coefficient μ of the compound for Cu $K\alpha$ is 99.7 cm⁻¹; for Mo $K\alpha$ it is 42.3 cm⁻¹. Thus the use of Cu $K\alpha$ radiation does not seriously worsen the absorption problem. We chose to use Cu $K\alpha$ radiation because: (1) we felt that the large unit cell in conjunction with Mo $K\alpha$ radiation might possibly present a problem of overlapping data, especially if the balanced filter technique were used; (2) we felt that if only a β filter were to be employed, then the data set would probably be more reliable if Cu $K\alpha$ rather than Mo $K\alpha$ radiation were employed. This is in keeping with general experience that proper correction for background is more difficult with Mo $K\alpha$ than with Cu $K\alpha$ radiation.

Alignment of the diffractometer was achieved through the use of the crystal of $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$. This crystal was ideal for the purpose because of its small, spherical shape, because of its good scattering properties for Cu $K\alpha$, and because of the large unit cell size. The crystal was used as a probe for both the source and the counter and each of these had satisfactory forms. The mosaicity of the crystal, as judged by the narrow-source, open-counter ω scan through several strong reflections, was satisfyingly low.⁸ After alignment of the diffractometer, 20 reflections from the crystal were accurately centered through a very narrow vertical slit at a take-off angle of 0.5° . These observations formed the basis for the least-squares refinement of cell parameters and orientation. The refinement was effected in our program PICK for the CDC 3400 computer. The essential logic of this program is based on MODE 1, written by W. C. Hamilton. The cell parameters derived by this process should be looked upon as instrumental cell parameters, as they may be affected by systematic errors arising from imperfections in the diffractometer, from alignment errors, and from crystal-centering errors. Nevertheless, their accuracy is sufficiently high to leave the derived bond distances unaffected.

Intensity data were collected at a take-off angle of 1.3° . At this angle, the peak intensity of a typical strong reflection is 70% of the maximum value as a function of take-off angle. The use of a small take-off angle, while decreasing the integrated count, does ensure adequate resolution and a smaller scan range. The receiving aperture size selected to minimize extraneous background was 5.7 mm wide by 4.0 mm high. The aperture was positioned 21 cm from the crystal. The data were collected by the θ - 2θ scan technique at a scan rate of $2.0^\circ/\text{min}$. The scan range for all reflections was 1.85° in 2θ , from -0.90 to $+0.95^\circ$ from the calculated 2θ value. All scans were recorded on a chart recorder; this provided visual evidence for proper peak shape, reflection centering in 2θ , and nonoverlap of adjacent reflections. Stationary counter background counts of 10 sec were taken at each end of the scan range. Under these conditions approximately 30 reflections could be scanned per hour. The Cu $K\alpha$ beam was filtered through 1.0-mil Ni foil after diffraction from the crystal. The Picker system automatically inserts attenuators if the intensity of the diffracted beam exceeds about 7000 counts/sec during the scan. Copper foils were used as attenuators, the thickness being chosen to give attenuator factors of approximately 2.5. The pulse height analyzer was set for approximately a 90% window, centered on the Cu $K\alpha$ peak.

As a check on electronic and crystal stability during the period of data collection, the intensities of three standard reflections were measured periodically. No systematic drift in these standards was observed. As a further check on electronic and crystal stability and in order to ensure a better data set, all four equivalent forms of this centrosymmetric monoclinic crystal (hkl , $\bar{h}\bar{k}l$, $h\bar{k}l$, and $\bar{h}k\bar{l}$) were measured. Since the program PICK orders the reflections in an attempt to minimize slewing times of the drive motors, the given equivalent forms of a reflection typically were collected at widely varying times during the period of data collection. A total of 6866 intensities were measured within the sphere $\theta(\text{Cu } K\alpha_1) \leq 38.25^\circ$. (Past this point only a small fraction of the intensities was significantly above background.)

All data processing was carried out with the program PICKOUT, written by R. J. D. The data were first corrected for background; here it is assumed that the background can be approximated by a straight line between the two measured background points. The corrected intensities were next assigned standard deviations according to the formula

$$\sigma(I) = [CT + 0.25(t_0/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained in a scan of time t_0 , B_1 and B_2 are the background counts each obtained in time t_b , and $I = CT - 0.5(t_0/t_b) \cdot (B_1 + B_2)$. The value of p was selected as 0.03. The inclusion of the last term⁹ in the expression for $\sigma(I)$ may be considered an "ignorance" factor. We are, in fact, ignorant of exactly what effects are operating

(8) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(9) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

to cause variations in intensity between, for example, hkl and $\bar{h}\bar{k}\bar{l}$ in a centrosymmetric nonabsorbing crystal, but it is known that such variations do occur. Presumably all nonisotropic effects, including extinction, will contribute to such variations. This term in the expression is necessary if one is to prevent ridiculously high weight being given to strong reflections. The value for p of 0.03 was a guess on our part. The final value of the standard deviation of an observation of unit weight (1.53) indicates that a value of p of 0.04–0.05 would have been preferable. The values of I and $\sigma(I)$ were next corrected for Lorentz-polarization effects and for absorption. The absorption correction was based on an average calculated value of μR of 1.00. The equivalent forms were then sorted together and the individual values of F^2 , the square of the structure amplitude, were averaged. The standard deviation of F^2 , $\sigma(F^2)$, was taken either as the average of the individual standard deviations of the equivalent forms or as a value estimated from the range of the F^2 values of the equivalent forms, whichever was larger. When the range estimate exceeded the average estimate by more than a factor of 2.0, the individual measurements were reexamined for possible setting errors of the diffractometer. Only a few such cases were found throughout the 6866 measurements. The total number of independent reflections thus obtained was 1792. Of these, 243 were less than their standard deviations.

At least one source of systematic error is apparent on examination of the agreement between the F^2 values of the equivalent forms. The forms hkl and $\bar{h}\bar{k}\bar{l}$ agree better with their negative forms than they do with one another. Presumably this is because the crystal was not a perfect sphere. There is perhaps a 10% difference between minimum and maximum radii; in the extreme case this could result in a 10% variation in F^2 . In general the variation between F^2 of hkl and F^2 of $\bar{h}\bar{k}\bar{l}$ was considerably less than 10%.

Solution and Refinement of the Structure

Initial values for all atomic coordinates were obtained by the usual Patterson and Fourier techniques.¹⁰ The position of the Re atom was determined from the Patterson function; a subsequent difference Fourier led to positions for the P, Cl, and N atoms; a second difference Fourier, based on refined positions for these heavy atoms, led to the positions of all the remaining nonhydrogen atoms and enabled us to distinguish P from Cl on the basis of coordination geometry. Initial least-squares refinements were carried out on F , rather than on F^2 ; that is, the function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ is the observed structure amplitude, $|F_c|$ the calculated structure amplitude, and 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 Ibers¹¹ were used for P, Cl, C, N, and H and

those of Cromer and Waber¹² for Re. The effects of anomalous dispersion were included in F_c ;¹³ the values of f' and f'' for Re, Cl, and P were those given by Cromer.¹⁴

Initially all atoms were assigned variable isotropic thermal parameters and after three cycles of refinement of the 149 variables (scale factor plus three positional and one thermal parameter per atom) the usual discrepancy factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and R_2 (or weighted R factor) $= (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ were 6.5 and 7.3%, respectively. Two further cycles in which the rhenium atom was assigned variable anisotropic thermal parameters lowered R_1 and R_2 to 5.1 and 6.0%. A difference Fourier at this point showed some signs of anisotropic thermal motion of the phosphorus and chlorine atoms. In line with our previous contention¹⁵ that it is desirable to put information into the least-squares model that is known with greater accuracy than can be determined from the observations and also in order to save computer time and storage, ensuing refinements were carried out with the phenyl groups restricted to their well-known geometry (D_{6h} symmetry, C-C = 1.392 Å). These calculations were performed in the program NUGLS, which is an amalgamation of the programs JGLS¹⁵ of J. A. I. written at Brookhaven National Laboratory and of ORFLSD of R. J. D.¹⁶ written at the University of Wisconsin. The program NUGLS uses the same coordinate system described previously;¹⁵ it differs from JGLS principally in the use of exact expressions for the derivatives and in the option to vary separately the isotropic thermal parameters of each atom in the rigid group. In order to permit comparison of the group model for the phenyl rings with the individual atom model, the first two cycles of the group refinement were carried out with isotropic thermal parameters for all atoms. Comparison of the weighted R factor of 7.6% thus obtained with that of 7.3% from the individual refinement indicates¹⁷ that the individual model is significantly better than the group model. This statistical test is based on the premise that there are only random errors in the data. It seems to us more reasonable to conclude that there are residual systematic errors in the data that invalidate the statistical test, rather than conclude that the phenyl rings are significantly distorted. A cycle of group refinement in which anisotropic thermal parameters were assigned to the Re, Cl, and P atoms reduced the R factors to 5.4 and 5.9%. Next the C-H distance in the phenyl group was assumed to be 1.08 Å, and the phenyl hydrogen atoms were included in the calculations as fixed contributions to F_c ; the resultant R factors were 5.1 and 5.7%, respectively. Reliable positions for the ethyl hydrogen atoms could not be obtained from difference maps and so contributions to F_c from these atoms were ignored. A refinement on F , based on the weights

(10) In addition to the various local programs for the CDC 3400 described in the text, the programs used in this work were local modifications of Zalkin's FORDAP Fourier program and of the Busing-Levy ORFEE error function program.

(11) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

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

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

(15) S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965).

(16) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

(17) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

TABLE I
 POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$

Atom	x	y	z	β_{11}^a or $B_1, \text{Å}^2$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}			
Re	0.22715 (5) ^b	0.04334 (7)	0.14000 (5)	0.00488 (5)	0.00932 (10)	0.00524 (6)	0.00074 (6)	0.00334 (5)	-0.00005 (5)			
Cl ₁	0.1985 (3)	0.0389 (4)	0.2568 (3)	0.0070 (3)	0.0155 (6)	0.0064 (3)	0.0016 (4)	0.0048 (3)	0.0002 (4)			
Cl ₂	0.3599 (3)	0.1584 (4)	0.2504 (3)	0.0056 (3)	0.0119 (5)	0.0062 (3)	0.0001 (3)	0.0028 (2)	-0.0013 (3)			
P ₁	0.3071 (3)	-0.1401 (4)	0.2063 (3)	0.0062 (3)	0.0084 (5)	0.0062 (3)	0.0000 (3)	0.0044 (3)	0.0005 (3)			
P ₂	0.2853 (3)	0.0812 (4)	0.0500 (3)	0.0042 (2)	0.0072 (5)	0.0052 (3)	0.0000 (3)	0.0029 (2)	-0.0006 (3)			
P ₃	0.1419 (3)	0.2234 (4)	0.0920 (3)	0.0045 (2)	0.0097 (5)	0.0052 (3)	0.0005 (3)	0.0030 (2)	-0.0008 (3)			
N	0.1360 (7)	-0.0347 (10)	0.0579 (7)	4.0 (3)								
P ₁ E ₁ C ₁ ^c	0.4156 (9)	-0.1354 (14)	0.3058 (10)	4.6 (4)								
P ₁ E ₁ C ₂	0.4139 (10)	-0.0857 (16)	0.3856 (11)	6.8 (5)								
P ₁ E ₂ C ₁	0.2377 (12)	-0.2279 (18)	0.2332 (13)	8.7 (6)								
P ₁ E ₂ C ₂	0.2734 (15)	-0.3394 (23)	0.2642 (16)	12.7 (8)								
P ₂ E ₁ C ₁	0.3222 (9)	0.2354 (14)	0.0581 (10)	4.9 (4)								
P ₂ E ₁ C ₂	0.3570 (10)	0.2615 (15)	-0.0023 (11)	6.0 (4)								
P ₂ E ₂ C ₁	0.2100 (9)	0.0716 (13)	-0.0706 (10)	4.2 (4)								
P ₂ E ₂ C ₂	0.1597 (10)	-0.0460 (15)	-0.1052 (11)	6.3 (5)								
P ₃ E ₁ C ₁	0.1962 (9)	0.3596 (14)	0.1491 (10)	5.6 (4)								
P ₃ E ₁ C ₂	0.2180 (10)	0.3590 (15)	0.2457 (11)	6.4 (5)								
P ₃ E ₂ C ₁	0.0479 (10)	0.2119 (15)	0.1036 (10)	5.9 (4)								
P ₃ E ₂ C ₂	-0.0058 (10)	0.3277 (15)	0.0732 (11)	6.2 (5)								
Group	x_c^d	y_c	z_c	δ	ϵ	η	$B_1, \text{Å}^2$	$B_2, \text{Å}^2$	$B_3, \text{Å}^2$	$B_4, \text{Å}^2$	$B_5, \text{Å}^2$	$B_6, \text{Å}^2$
P ₁ R ₁	0.3199 (5)	-0.3195 (6)	0.0779 (5)	-1.655 (7)	-3.027 (7)	-0.849 (6)	4.8 (4)	6.0 (4)	6.1 (4)	6.3 (4)	6.0 (4)	5.4 (4)
P ₂ R ₁	0.4554 (4)	-0.0538 (6)	0.0916 (5)	2.247 (11)	2.224 (6)	-2.641 (11)	4.2 (4)	5.2 (4)	5.3 (4)	5.4 (4)	5.7 (4)	4.9 (4)
P ₃ R ₁	0.0515 (4)	0.2729 (7)	-0.1122 (5)	2.564 (6)	-3.009 (7)	-1.112 (6)	4.1 (4)	5.0 (4)	6.4 (5)	6.8 (5)	6.6 (5)	5.4 (4)

^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 P₁E₁C₁ is carbon atom 1 on ethyl group 1 attached to phosphorus 1, etc. P₁R₁ is the phenyl ring attached to phosphorus 1. ^d 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: see ref 15; 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 C₁ is attached to P; C₄ is *para* to C₁.

described previously, differs from a refinement on F^2 , with weights taken as $1/\sigma^2(F^2)$, insofar as F_o is not identical with F_c . It seems to us that this latter refinement procedure is to be preferred, if only because the F^2 values are more closely related to the observables than are the F values. Accordingly, in a final round of calculations the quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$, with w taken as $1/\sigma^2(F^2)$. In this final cycle only four positional parameters and the scale factor shifted by more than one standard deviation, with the largest shift of a positional parameter being 1.5 standard deviations. The final values of R_1 and R_2 (based on F^2) for these parameters are 7.0 and 11.3%. These parameters (Table I) lead to a value of R_1 (based on F) of 5.1%.

Through the refinement, the temperature factors of two of the ethyl carbon atoms (ethyl group 2 of phosphorus 1) were disturbingly high and the bond length of 1.42 Å between these atoms compares unfavorably with expectation and with bond lengths of 1.57–1.58 Å in the other five ethyl groups. In order to test the possibility that the positions of these atoms represent a false minimum in the least-squares refinement, a difference Fourier based on structure factors calculated without contributions from the suspected ethyl group was computed at the conclusion of the isotropic refinement. The two largest peaks on this map, of heights 2.4 and 1.6 e⁻/Å³, were at the positions of the carbon atoms omitted. The next highest peak (0.6 e⁻/Å³) was in the immediate vicinity of the group. On a final difference Fourier map, computed at the end of the refinement on F^2 , this peak was the highest feature at 1.0 e⁻/Å³. A disordered model in which this peak represents an alternate position for the β -carbon atom and with the two α -carbon atoms each slightly displaced

 TABLE II
 DERIVED PARAMETERS FOR GROUP CARBON ATOMS

	x	y	z
P ₁ R ₁			
C ₁	0.3172 (8) ^a	-0.2391 (8)	0.1335 (7)
C ₂	0.2428 (6)	-0.2706 (10)	0.0562 (8)
C ₃	0.2454 (6)	-0.3511 (10)	0.0006 (6)
C ₄	0.3226 (8)	-0.4000 (9)	0.0223 (7)
C ₅	0.3971 (6)	-0.3685 (10)	0.0996 (8)
C ₆	0.3944 (6)	-0.2880 (10)	0.1552 (6)
P ₂ R ₁			
C ₁	0.3805 (7)	0.0001 (17)	0.0725 (6)
C ₂	0.4543 (8)	0.0130 (9)	0.1547 (6)
C ₃	0.5292 (5)	-0.0409 (14)	0.1738 (6)
C ₄	0.5303 (7)	-0.1076 (17)	0.1107 (7)
C ₅	0.4566 (8)	-0.1205 (9)	0.0284 (6)
C ₆	0.3817 (5)	-0.0666 (14)	0.0094 (5)
P ₃ R ₁			
C ₁	0.0901 (6)	0.2557 (10)	-0.0228 (5)
C ₂	0.1123 (6)	0.3513 (8)	-0.0534 (7)
C ₃	0.0737 (7)	0.3685 (9)	-0.1427 (8)
C ₄	0.0130 (7)	0.2902 (11)	-0.2015 (5)
C ₅	-0.0092 (6)	0.1946 (10)	-0.1710 (7)
C ₆	0.0294 (6)	0.1774 (8)	-0.0816 (8)

^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 Å).

from the refined position of the single α -carbon atom is consistent with the difference maps. In particular, the peak for the α -carbon atom on the difference map in which the ethyl group was omitted is distinctly elongated in the direction of the suggested displacements. Attempts to define this disorder more fully by structure factor calculations were inconclusive. We can only say that we do not take seriously either the temperature factors or the carbon-carbon distance for this group.

TABLE III
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (X10) (IN ELECTRONS) FOR ReNC12(P(C2H5)2C6H5)3

Table with multiple columns for observed and calculated structure amplitudes. Columns are labeled with 'H L OBS CALC' and contain numerical values. The table is organized into sections for different reflections, such as 'K=0', 'K=3', 'K=5', 'K=6', 'K=7', 'K=8', 'K=9', 'K=10', 'K=11', 'K=12', 'K=13', 'K=14', 'K=15', 'K=16', 'K=17', 'K=18', 'K=19', 'K=20', 'K=21', 'K=22', 'K=23', 'K=24', 'K=25', 'K=26', 'K=27', 'K=28', 'K=29', 'K=30', 'K=31', 'K=32', 'K=33', 'K=34', 'K=35', 'K=36', 'K=37', 'K=38', 'K=39', 'K=40', 'K=41', 'K=42', 'K=43', 'K=44', 'K=45', 'K=46', 'K=47', 'K=48', 'K=49', 'K=50', 'K=51', 'K=52', 'K=53', 'K=54', 'K=55', 'K=56', 'K=57', 'K=58', 'K=59', 'K=60', 'K=61', 'K=62', 'K=63', 'K=64', 'K=65', 'K=66', 'K=67', 'K=68', 'K=69', 'K=70', 'K=71', 'K=72', 'K=73', 'K=74', 'K=75', 'K=76', 'K=77', 'K=78', 'K=79', 'K=80', 'K=81', 'K=82', 'K=83', 'K=84', 'K=85', 'K=86', 'K=87', 'K=88', 'K=89', 'K=90', 'K=91', 'K=92', 'K=93', 'K=94', 'K=95', 'K=96', 'K=97', 'K=98', 'K=99', 'K=100'. Each section contains two columns of data: 'OBS' (observed) and 'CALC' (calculated).

Yet a slightly simplified description of this group in terms of an ordered model, as used in our refinements, should have no effect on the parameters of the other atoms. These other parameters are essentially uncorrelated with those of the selected ethyl group. Comparison of the final values of F_o and F_c did not

suggest to us that such a correction for secondary extinction was necessary. The positional, thermal, and group parameters derived from the last cycle of least-squares refinement on F^2 are presented in Table I, along with the corresponding standard deviations in these parameters as esti-

mated from the inverse matrix. The positional parameters of the group carbon atoms which may be derived from the data of Table I are presented in Table II. The final values of $10F_o$ and $10F_c$ (in electrons) are presented in Table III. All observations, including those in which F_o^2 was less than $\sigma(F_o^2)$, were used in the refinements and are listed in Table III.

Description of the Structure

The crystal structure, as defined by the unit cell dimensions, symmetry operations, and parameters of Table I, consists of the packing of monomeric molecular units. In Figure 1 the over-all molecular structure is displayed; in Figure 2 only the inner coordination

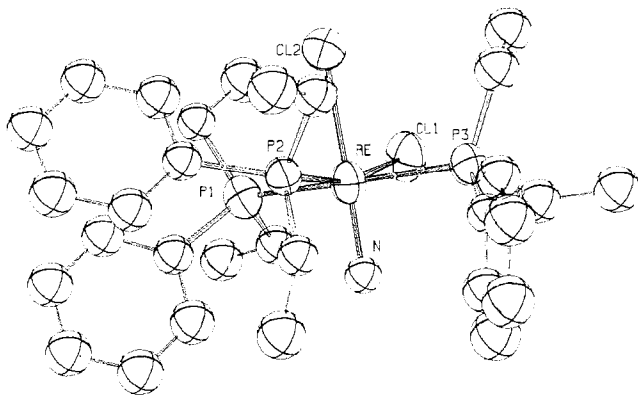


Figure 1.—A perspective drawing of the molecular structure of $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$.

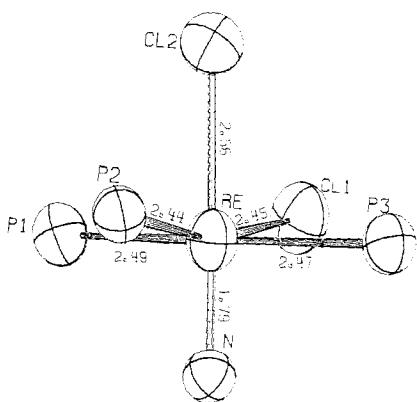


Figure 2.—A perspective drawing of the inner coordination sphere of $\text{ReNCl}_2[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3$.

about the Re atom is shown. The coordination about Re is that of a distorted octahedron. Principal intramolecular distances and angles and their estimated standard deviations, as derived from the data of Table I and the correlation matrix, are given in Table IV. The intermolecular distances appear to be normal and so only the closest intermolecular approaches to Re and N are given in Table IV.

The octahedral configuration found is one of the possible configurations deduced by Chatt, *et al.*,² primarily on the basis of dipole moment measurements. Their other possible configuration would have *trans* halogen atoms and N *trans* to P; that is, N and Cl₁ would be interchanged.

TABLE IV
SELECTED DISTANCES (Å) AND ANGLES (DEGREES)

—Intramolecular distance—		—Angle—	
Re-Cl ₁	2.454 (4)	Cl ₁ -Re-Cl ₂	84.36 (15)
Re-Cl ₂	2.563 (4)	Cl ₁ -Re-P ₁	85.17 (15)
Re-P ₁	2.490 (5)	Cl ₁ -Re-P ₂	165.16 (15)
Re-P ₂	2.442 (4)	Cl ₁ -Re-P ₃	85.64 (15)
Re-P ₃	2.469 (5)	Cl ₁ -Re-N	99.2 (4)
Re-N	1.788 (11)	Cl ₂ -Re-P ₁	89.08 (15)
Cl ₁ -Cl ₂	3.370 (6)	Cl ₂ -Re-P ₂	80.90 (14)
Cl ₁ -P ₁	3.346 (6)	Cl ₂ -Re-P ₃	90.63 (14)
Cl ₁ -P ₂	4.856 (6)	Cl ₁ -Re-N	176.4 (4)
Cl ₁ -P ₃	3.346 (7)	P ₁ -Re-P ₂	96.29 (14)
Cl ₁ -N	3.258 (12)	P ₁ -Re-P ₃	170.80 (14)
Cl ₂ -P ₁	3.545 (6)	P ₁ -Re-N	91.8 (4)
Cl ₂ -P ₂	3.249 (6)	P ₂ -Re-P ₃	92.74 (14)
Cl ₂ -P ₃	3.578 (6)	P ₂ -Re-N	95.6 (4)
Cl ₂ -N	4.349 (12)	P ₃ -Re-N	89.1 (4)
P ₁ -P ₂	3.674 (6)	Re-P ₁ -P ₁ E ₁ C ₁	120.2 (5)
P ₁ -P ₃	4.943 (6)	Re-P ₁ -P ₁ E ₂ C ₁	105.2 (6) ^a
P ₁ -N	3.110 (12)	Re-P ₂ -P ₂ E ₁ C ₁	113.1 (5)
P ₂ -P ₃	3.555 (6)	Re-P ₂ -P ₂ E ₂ C ₁	116.9 (4)
P ₂ -N	3.164 (11)	Re-P ₃ -P ₃ E ₁ C ₁	117.2 (5)
P ₃ -N	3.024 (13)	Re-P ₃ -P ₃ E ₂ C ₁	111.4 (6)
P ₁ -P ₁ E ₁ C ₁	1.854 (15)	P ₁ -P ₁ E ₁ C ₁ -P ₁ E ₁ C ₂	110.8 (1.0)
P ₁ -P ₁ E ₂ C ₁	1.902 (19)	P ₁ -P ₁ E ₂ C ₁ -P ₁ E ₂ C ₂	110.1 (1.6)
P ₁ -P ₁ R ₁ C ₁	1.833 (12)	P ₂ -P ₂ E ₁ C ₁ -P ₂ E ₁ C ₂	113.3 (1.1)
P ₂ -P ₂ E ₁ C ₁	1.880 (16)	P ₂ -P ₂ E ₂ C ₁ -P ₂ E ₂ C ₂	115.5 (1.1)
P ₂ -P ₂ E ₂ C ₁	1.866 (15)	P ₃ -P ₃ E ₁ C ₁ -P ₃ E ₁ C ₂	110.8 (1.2)
P ₂ -P ₂ R ₁ C ₁	1.848 (18)	P ₃ -P ₃ E ₂ C ₁ -P ₃ E ₂ C ₂	110.9 (1.2)
P ₃ -P ₃ E ₁ C ₁	1.854 (17)	—P ₁ CPC angles—	
P ₃ -P ₃ E ₂ C ₁	1.880 (15)	E ₁ -E ₂	107.6 (6)
P ₃ -P ₃ R ₁ C ₁	1.806 (14)	E ₁ -R ₁	103.8 (6)
P ₁ E ₁ C ₁ -P ₁ E ₁ C ₂	1.576 (20)	E ₂ -R ₁	101.9 (6)
P ₁ E ₂ C ₁ -P ₁ E ₂ C ₂	1.417 (28) ^a	—P ₂ CPC angles—	
P ₂ E ₁ C ₁ -P ₂ E ₁ C ₂	1.578 (20)	E ₁ -E ₂	99.2 (7)
P ₂ E ₂ C ₁ -P ₂ E ₂ C ₂	1.573 (20)	E ₁ -R ₁	101.1 (7)
P ₃ E ₁ C ₁ -P ₃ E ₁ C ₂	1.577 (20)	E ₂ -R ₁	104.9 (7)
P ₃ E ₂ C ₁ -P ₃ E ₂ C ₂	1.578 (21)	—P ₃ CPC angles—	
—Intermolecular distance—		E ₁ -E ₂	105.0 (7)
Re-Re	≥ 7.236	E ₁ -R ₁	105.3 (7)
Re-P ₁ E ₂ C ₁	3.507 (20) ^b	E ₂ -R ₁	101.2 (7)
N-P ₃ R ₁ H ₆	2.68 ^b		

^a See discussion of this P₁E₂ group in the section "Solution and Refinement of the Structure." ^b This is the closest intermolecular approach to the first atom named.

That the structure found here is distorted can be appreciated from the figures, from Table IV, and from Table V where data on the best weighted least-squares planes¹⁸ are given. The atoms Cl₁, Cl₂, P₂, and N are essentially coplanar and these atoms, together with Re, are nearly coplanar. There are very significant deviations of atoms from the other four planes described in Table V.

The P and Cl ligands are loosely bound to Re. Thus the Re-P distances, which range from 2.44 to 2.49 Å, are long compared with those found recently in a variety of second- and third-row transition metal complexes containing phosphines (Rh-P = 2.32 Å in RhH(CO)(P(C₆H₅)₃)₃;^{15,19} Ir-P = 2.36, 2.37 Å in IrO₂Cl(CO)(P(C₆H₅)₃)₂²⁰ and 2.33, 2.36 Å in Ir(SO₂)Cl(CO)(P(C₆H₅)₃)₂;²¹ Pt-P = 2.26 Å in PtHBr(P(C₆H₅)₃)₂²²

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TABLE V
BEST WEIGHTED LEAST-SQUARES PLANES
Equations of Planes of the Form $AX + BY + CZ = D$
(Monoclinic Coordinates)

Atoms	Plane no.	A	B	C	D
Cl ₁ , Cl ₂ , P ₂ , N	1	7.423	-9.876	1.089	1.375
Re, Cl ₁ , Cl ₂ , P ₂ , N	2	7.580	-9.793	1.137	1.454
Cl ₁ , P ₁ , P ₂ , P ₃	3	9.455	6.062	5.505	3.347
Re, Cl ₁ , P ₁ , P ₂ , P ₃	4	9.447	6.047	5.530	3.202
Cl ₂ , P ₁ , P ₃ , N	5	13.379	0.511	-17.688	0.431
Re, Cl ₂ , P ₁ , P ₃ , N	6	13.887	0.799	-17.476	0.732

Distances of Atoms from Planes (A)

Atom	Plane no.					
	1	2	3	4	5	6
Re		0.0025 (8)		-0.0198 (8)		0.0105 (7)
Cl ₁	-0.006 (5)	-0.039 (5)	0.180 (5)	0.329 (5)		
Cl ₂	0.005 (5)	0.008 (5)			0.036 (4)	0.015 (4)
P ₁			-0.157 (5)	-0.007 (5)	-0.044 (4)	-0.184 (4)
P ₂	-0.005 (4)	-0.030 (4)	0.118 (4)	0.261 (4)		
P ₃			-0.145 (4)	-0.003 (4)	-0.046 (4)	-0.193 (4)
N	0.041 (11)	-0.017 (11)			0.346 (11)	0.117 (11)

and in $\text{PtHCl}(\text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2)_2^{23}$, but they do agree well with those of 2.45 and 2.48 Å found in $\text{ReOCl}_3(\text{P}(\text{C}_2\text{H}_5)_2\text{-C}_6\text{H}_5)_2$.⁵ The last complex, which is also distorted octahedral, is closely related to the present structure and may be derived from it by replacing N by O and P₂ by Cl. Although the equatorial Re-Cl distance of 2.45 Å in the present structure agrees reasonably well with the Re-Cl distances of 2.41-2.47 Å in $\text{ReOCl}_3\text{-}(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$, all of these distances must be considered long. Thus the Re-Cl distance in the $\text{Re}_2\text{O-Cl}_{10}^{4-}$ ion²⁴ is 2.38 Å and in an early determination the Re-Cl distance in the ReCl_6^{2-} ion is reported to be 2.37 Å.²⁵ Moreover, the equatorial Re-Cl distance in the present structure and the Re-Cl distances in the related oxo structure are in the range of Re-Br distances found recently in several octahedral complexes [$\text{Re-Br} = 2.51$ Å in $((\text{C}_2\text{H}_5)_4\text{N})(\text{ReBr}_4\text{O}(\text{H}_2\text{O}))$,⁶ $\text{Re-Br} = 2.43, 2.48, 2.49, 2.51$ Å in $((\text{C}_6\text{H}_5)_4\text{As})(\text{ReBr}_4\text{O}(\text{CH}_3\text{CN}))$], although normally the M-Br distance is some 0.10-0.15 Å longer than the M-Cl distance. To emphasize further that these Re-Cl distances are long, let us compare them with the Pt-halogen distances in the square-planar Pt complexes where the halogen is *trans* to H. We find a Pt-Cl distance of 2.42 Å in $\text{PtHCl}(\text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2)_2^{23}$ and a Pt-Br distance of 2.56 Å in $\text{PtHBr}(\text{P}(\text{C}_2\text{H}_5)_2)_2$.²² These distances are generally considered long and the lengthening is consistent with the *trans* effect of the H atom. Note that in the present compound the Re-Cl distance of 2.563 Å *trans* to N is some 0.10 Å longer than any we have been discussing and any of which we are aware. Clearly, the N atom has exerted a very strong *trans* effect on the Cl atom. In fact, one can rationalize the general lengthening of the Re-P and Re-Cl bonds on the basis of a large donation of electrons from N to Re with the general result of electrostatic repulsion among the ligands.

The P-C distance and C-P-C angles are well within the range usually found in PR_3 groups. There is some

indication from the data of Table IV that the P-aryl distance is slightly shorter than the P-alkyl distance.

A discussion of the Re-N bond length will be reserved for the following paper. However, it is appropriate to compare the structure found here with the few other reported structures of metal-nitrido complexes. The inclusive list appears to be KOsO_3N ,²⁶ K_2OsNCl_5 ,²⁷ and $\text{K}(\text{OsNBr}_4(\text{H}_2\text{O}))\cdot\text{H}_2\text{O}$.²⁷ The very early work on the OsO_3N^- ion²⁶ suggests that the Os-O (or N) distance is 1.62 Å; the error in this determination, in which N could not be distinguished from O, is probably in excess of 0.1 Å. The results on K_2OsNCl_5 are most surprising. The OsNCl_5^{2-} ion is octahedral. The basal Os-Cl distances are 2.40 Å, the Os-N distance is 1.61 Å, and the Os-Cl distance *trans* to N is 2.16 Å. The structure was solved by projection methods and was apparently not refined. One would guess that the limits of error are approximately 0.05 Å on Os-Cl and greater than 0.10 Å on Os-N. Nevertheless, the Os-Cl bond *trans* to N is apparently some 0.2 Å shorter than normal, whereas the Re-Cl bond *trans* to N in the present structure is perhaps some 0.2 Å longer than normal. An explanation for this extreme shortening of the Os-Cl bond has been offered²⁸ in terms of the formation of δ bonds between Os and Cl. Yet if this explanation were correct, the same effect should occur in the present structure since Os(VI) and Re(V) are isoelectronic. A redetermination of the structure of K_2OsNCl_5 is now underway in these laboratories. No details are available on the structure of $\text{K}(\text{OsNBr}_4(\text{H}_2\text{O}))\cdot\text{H}_2\text{O}$,²⁷ except that the Os-N distance is supposed to be 1.61 Å.

Thermal Motions of the Atoms

In Table VI we list the mean-square amplitudes of vibration of those atoms which were refined anisotropically. The anisotropy is small. The directions of vibration can be seen in Figure 2. The data of Table I on the individual, isotropic thermal parameters of the

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TABLE VI
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)^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 C₁ atoms attached to P and greatest for the C₄ atoms *trans* to C₁. 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

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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 Å. This small decrease (0.006 Å) 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.

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Studies of Metal-Nitrogen Multiple Bonds. II. The Crystal and Molecular Structure of Nitridodichlorobis(triphenylphosphine)rhenium(V), ReNCl₂(P(C₆H₅)₃)₂

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The crystal and molecular structure of nitridodichlorobis(triphenylphosphine)rhenium(V), ReNCl₂(P(C₆H₅)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}⁸-I2/a of the monoclinic system, with four molecules in a cell of dimensions *a* = 15.71, *b* = 9.53, *c* = 22.17 Å; β = 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 Å. Although the Re-Cl and Re-N distances differ markedly from those found in the closely related six-coordinated Re(V) complex, ReNCl₂(P(C₂H₅)₂C₆H₅)₂, 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), ReNCl₂(P(C₆H₅)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 ReNCl₂(PR₃)₃, in which the Re is six-coordinated, by removal of one PR₃ 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 series¹ described the structure of ReNCl₂(P(C₂H₅)₂C₆H₅)₂. Second, five-coordinate transition metal complexes are of interest in themselves, since no consistent

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