the spin ground state of the complex. Whereas the generally accepted Ni^{2+} octahedral spin-triplet radius is 1.39 Å,[23] the low-spin radius of Ni^{2+} in square-planar complexes is probably around 1.18–1.20 Å. Therefore, the 2.267-Å value which we observe in $Ni(TSP)Cl^+$ is slightly longer than but in reasonable agreement with a calculated Ni–S bond distance of 2.22–2.24 Å using the proper covalent radii. We are therefore led to believe that there is minimal metal–sulfur π bonding in complexes of this type containing coordinated thioethers. This conclusion is affirmed by the recent structure determination of the related complex $Ni(DSP)I_2$ (DSP = bis(*o*-methylthiophenyl)phenylphosphine) by Meek and Ibers in which a value of 2.19 Å is observed for the basal Ni–S distance.[24] In addition, an examination of the bond distances and angles around the sulfur atoms in $Ni(TSP)Cl^+$ clearly indicates an approximate sp^3 hybridization for the coordinated thioether which is entirely consistent with the notion of very limited metal–sulfur π bonding. Any arguments which suggest the existence of considerable metal–sulfur π bonding must rely on *extensive* involvement of the vacant sulfur 3d orbitals which, although possible, does not seem likely.

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation (Grant No. GP-8079). We wish to thank Professor Devon Meek of The Ohio State University for the generous supply of the $[Ni(TSP)Cl][ClO_4]$ complex and for several very helpful and enlightening discussions. We also wish to thank Mr. G. P. Khare and Mr. Cortlandt Pierpont for their timely remarks in discussion. We are grateful to the National Science Foundation (Grant GP-4825) and Brown University for support of the computer time required for this work.

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[23] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7, Table 7-16.

[24] D. W. Meek, private communication; D. W. Meek and J. A. Ibers, *Inorg. Chem.*, in press.

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The Crystal Structure of Trichloroamminebis(triphenylphosphine)osmium(III), $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

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Received October 17, 1968

The yellow-orange product obtained from the reaction of oxotrichlorobis(triphenylphosphine)osmium(V) with hydrazine dihydrochloride in refluxing ethanol–water solutions and recrystallized from acetonitrile is shown, on the basis of a diffraction study, to be trichloroamminebis(triphenylphosphine)osmium(III), $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. The crystal structure has been determined from three-dimensional X-ray data collected by counter methods and has been refined using least-squares techniques to a final R factor, on F, of 3.2% for the 1554 independent reflections above background. The material crystallizes in the monoclinic space group $C_{2h}{}^6$-I2/a in a cell of dimensions a = 22.429 (8), b = 9.519 (3), c = 15.852 (5) Å, and β = 102.80 (2)°. The density of 1.69 g/cm³ calculated for four formula units in the cell agrees well with the observed density of 1.68 ± 0.01 g/cm³. The well-separated individual molecules are required crystallographically to possess C_2 symmetry. Imposition of C_2 symmetry requires that the ammine hydrogens be disordered, and an NH_3 group freely rotating about the Os–N bond was used as an approximation to this disorder. The configuration about the osmium atom is distorted octahedral with P atoms *trans* to one another and Cl atoms *trans* to one another in the basal plane and with the third Cl atom at the one vertex and the ammine group at the other. The only large deviation from an ideal octahedral configuration is a movement of the Cl atoms *cis* to N toward the nitrogen atom. The Os–N distance is 2.136 (9) Å, and the Os–P distance is 2.411 (2) Å. The Os–Cl distance *cis* to the N atom is not significantly different from the Os–Cl distance *trans* to the N atom, and the mean value of these distances is 2.362 (1) Å. The geometric details on this molecule are compared with previous results on aryl- and alkylimino complexes of Re and found to be explicable in terms of intramolecular nonbonded interactions.

Introduction

From a series of studies of closely related compounds containing metal–nitrogen multiple bonds[1–5] we concluded[5] that in these cases the variations in metal–ligand bond distances and in distortions about the central metal may be most easily understood in terms of nonbonded intramolecular interactions. In the course of attempts to prepare the nitrido complex $OsNCl_3(P(C_6H_5)_3)_2$, the phosphine analog of the $OsNCl_5{}^{2-}$ ion, Chatt and Paske[6] separated a paramagnetic compound of nearly the correct composition which exhibited N–H stretching bands in the infrared region of the spectrum. Although a dimeric complex is a possibility (*cf.* $(NH_3)_5RuNNRu(NH_3)_5{}^{4+}$ [7]), the most probable formulation of the compound was thought to be either $OsCl_3(NH)(P(C_6H_5)_3)_2$ or $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. The present

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

[2] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[3] D. Bright and J. A. Ibers, *ibid.*, **7**, 1099 (1968).

[4] D. Bright and J. A. Ibers, *ibid.*, **8**, 703 (1969).

[5] D. Bright and J. A. Ibers, *ibid.*, **8**, 709 (1969).

[6] J. Chatt and R. J. Paske, unpublished work.

[7] D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

investigation of this compound was undertaken for two reasons: first, to provide evidence on its nature and, second, to obtain geometrical details of the (presumed) monomeric compound for comparison with our previous results and with our predictions based on the notion that in complexes containing metal–nitrogen multiple bonding nonbonded interactions are of primary importance. On the basis of evidence reported here the compound is $OsCl_3(NH_3)(P(C_6H_5)_3)_2$, and its geometry is consistent with the ideas presented earlier.

Experimental Section

Preparations.—The following preparations were carried out in consultation with Professor J. Chatt. Details on the analyses and characterizations of these compounds will be presented separately.[8]

Oxotrichlorobis(triphenylphosphine)osmium(V).—A solution of triphenylphosphine, 5.00 g, in ethanol, 20 ml, was added to a solution of osmium tetroxide, 1.00 g, in ethanol, 30 ml, and concentrated hydrochloric acid, 5 ml. The mixture was heated under reflux for 20 min. The brown-orange precipitate was filtered off and washed with water, diethyl ether, and ethanol; yield 2.6 g.

Trichloroamminebis(triphenylphosphine)osmium(III).—Oxotrichlorobis(triphenylphosphine)osmium(V), 1.00 g, and hydrazine dihydrochloride, 0.60 g, were suspended in ethanol, 60 ml, and water, 10 ml, and heated under reflux, with stirring for 2 hr. The yellow-orange product was recrystallized from acetonitrile to yield orange prisms.

Collection and Reduction of the Intensity Data

Preliminary Weissenberg and precession photographs of the material showed monoclinic diffraction symmetry. The cell dimensions were determined from a least-squares refinement[1] of the setting angles of 21 reflections that had been carefully centered on a Picker four-circle automatic diffractometer at 22° using Cu Kα_1 radiation (λ 1.54056 Å). The results were: $a = 22.429$ (8), $b = 9.519$ (3), $c = 15.852$ (5) Å, and $\cos \beta = -0.2216$ (3).

The systematic absences observed on the films were hkl for $h + k + l$ odd and $h0l$ for h odd. These absences are consistent with either space group C_{2h}^6-I2/a or C_s^4-Ia. The density of 1.69 g/cm^3 calculated for four molecules of $OsCl_3(NH_3)(P(C_6H_5)_3)_2$ in the unit cell agrees well with the density 1.68 ± 0.01 g/cm^3 measured by suspending the crystals in aqueous potassium iodide. 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 parallel those described previously.[1] A crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm was selected. In preparation for an absorption correction, this crystal was carefully measured by means of a micrometer eyepiece and the indices of its faces were identified using an optical goniometer. The monoclinic forms developed on most of the crystals were $\{001\}$, $\{100\}$, and $\{011\}$. The crystal was then mounted on a Picker diffractometer with the c direction approximately coincident with the ϕ axis. Since c is not a symmetry axis, this mounting does not increase the probability of multiple-diffraction conditions. Open-counter, narrow-source ω scans through several strong reflections indicated that the mosaicity of the crystal was reasonably small, $\approx 0.1°$ in half-width.

The data were collected using Mo Kα radiation and the diffracted beams were filtered through 3 mils of Nb foil. The intensities were measured by the θ–2θ scan technique at a takeoff angle of 1.3°. At this angle the intensity of a reflection was about 80% of its maximum value as a function of takeoff angle. The crystal to counter distance was 35 cm, and the counter aperture was 5 mm^2. The scan range in 2θ was from $-0.65°$ from the Mo Kα_1 peak (λ 0.70930 Å) to $+0.65°$ from the Mo Kα_2 peak (λ 0.71359 Å). The scan rate was 1°/min and stationary-counter, stationary-crystal background counts of 10 sec each were taken at each end of the scan. Errors due to coincidence losses in counting were avoided by insertion of copper foil attenuators into the diffracted beam if its intensity exceeded 7000 counts/sec. The thicknesses of the attenuators were chosen to give attenuation factors of about 2.5.

Intensity data were collected from the independent hkl planes of the monoclinic form out to 2θ(Mo Kα_1) $\leq 41°$. Although some additional higher angle data could have been obtained, the present data set is sufficient to define the structure to high precision.

The data were processed in the manner described previously.[1,2] After initial correction for background, the standard deviation $\sigma(I)$ of the corrected intensity I was estimated using a value of $p = 0.03$.

The intensities were next corrected for Lorentz and polarization effects and then for absorption.[9] The calculated linear absorption coefficient for Mo Kα radiation was taken to be 44.7 cm^{-1}. (This coefficient varies negligibly whether the compound is assumed to be an imine or an ammine.) Transmission factors ranged from 0.42 to 0.59.

A total of 1670 independent reflections were measured. Of these the 116 which were found to have $I \leq 3\sigma(I)$ will be referred to as being below background.

Solution and Refinement of the Structure

In the least-squares refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight w is $1/\sigma^2(F_o)$. The estimated standard deviation of F_o, $\sigma(F_o)$, was taken as $\sigma(F_o^2)/2F_o$. The agreement factors R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$.

The scattering factors used for P, Cl, and N were taken from the usual tabulation,[10] and those for Os

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[8] J. Chatt, J. R. Dilworth, and G. J. Leigh, unpublished work; the preparation of $OsOCl_3(P(C_6H_5)_3)_2$ is described by J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc., A*, 2636 (1968).

[9] The programs used in this work were PICK and PICKOUT for generating and processing the data, NUCLS the group-refinement program, and local modifications of Hamilton's GONO absorption correction program, Zalkin's FORDAP Fourier summation program, the Busing–Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

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

were calculated by Cromer and Waber.[11] The hydrogen scattering factors were those of Stewart, *et al.*[12] The effects of anomalous scattering were taken into account in the structure factor calculations.[13] The values of $\Delta f'$ and $\Delta f''$ for Os, P, and Cl were those given by Cromer.[14]

The osmium atom was readily located from inspection of the three-dimensional Patterson function, and the remaining nonhydrogen atoms were located from subsequent difference Fourier syntheses. The positions of all of these atoms were consistent with the centrosymmetric space group I2/a, and the structure was refined in this space group for the remainder of the analysis. [The equivalent positions of I2/a are (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$) $\pm$ (x, y, z; $^1/_2 - x$, y, $\bar{z}$).] The agreement factors with all nonhydrogen atoms included with isotropic thermal parameters were $R_1 = 4.7\%$ and $R_2 = 6.1\%$. Addition of variable anisotropic thermal parameters for the nongroup, nonhydrogen atoms led to values of R_1 and R_2 of 3.5 and 4.8%, a highly significant improvement.[15]

The positions of the hydrogen atoms on the phenyl groups were next computed (C–H = 0.9 Å) and the fixed contributions of these atoms to F_c were included in an additional cycle of refinement. The resultant values of R_1 and R_2 were 3.2 and 4.3%.

At this stage the thermal ellipsoids obtained for the atoms which lie on the twofold axis (assuming the centrosymmetric space group I2/a) were carefully examined for anomalies, *e.g.*, excessive motion normal to the axis, which would suggest an improper choice of space group. No such anomalies were found. In addition, the thermal parameters of the ring carbon atoms were normal. If the true space group were Ia, then one would expect such carbon atoms to be superpositions of independent rings that had been falsely related by an assumed twofold axis and hence to exhibit excessive thermal motion. For these reasons we made no attempt to refine the structure in the noncentrosymmetric space group Ia.

In an attempt to decide on the composition of the material, a difference Fourier synthesis in the vicinity of the nitrogen atom was calculated. The only feature on the twofold axis was a peak of height 0.5 e$^-$/Å^3 about 0.5 Å from the N atom. In view of the anticipated quality of the data set, such a position is an unlikely one for the H atom in a possible Os–N–H bonding sequence but rather is suggestive of an Os–N–H_3 sequence, with the electron densities of the three off-axis hydrogen atoms overlapping on the axis. Additional evidence for the characterization of this compound as an ammine, rather than as an imine, comes from the Os–N distance, which at this stage of refinement was 2.15 Å. This is about what we would expect for an Os–NH_3 distance and is substantially longer than we would expect for an Os–NH distance on the basis of our earlier results where the Re–N distances in aryl- and alkylimino complexes of rhenium are less than 1.72 Å.[3,4]

Assumption of space group I2/a requires that the molecule possess C_2 symmetry and the NH_3 hydrogen atoms must therefore be disordered. The possible models for disorder lie between the following extremes: (1) an NH_3 group freely rotating about the Os–N bond, leading to a doughnut-shaped region of electron density, and (2) stationary hydrogen atoms with twofold disorder leading to six half-hydrogen peaks in the electron density arranged at 60° intervals around the twofold axis. The most probable model of disorder lies between these extremes and should give rise to six banana-shaped peaks in the electron density map. Since these peaks will overlap one another, it would be difficult to differentiate between such a model and that of the free rotor. The actual difference Fourier map exhibited electron density peaks that were definitely inconsistent with a twofold disorder of stationary hydrogen atoms. Consequently a Fourier synthesis was computed using the calculated coefficients for a freely rotating NH_3 group.[16] This map reproduced the observed difference Fourier map in the vicinity of the N atom very well indeed, including the single peak of height 0.5 e$^-$/Å^3 on the twofold axis. A cycle of least-squares refinement with the H atoms of a freely rotating NH_3 group (N–H = 0.9 Å, ∠Os–N–H = 109.5°, B = 5 Å^2) included as fixed contributions to F_c gave agreement factors $R_1 = 3.2$ and $R_2 = 4.1\%$. During this final cycle of refinement, no parameter shifted by more than one estimated standard deviation. The over-all improvement in agreement factors as a result of inclusion of the H atoms of the NH_3 group appears to be slight. However, since these H atoms do not contribute significantly to the high-angle data, it is more instructive to consider their effect on the agreement factors for the low-angle data. For that portion of the data with $\lambda^{-1} \sin \theta$ less than 0.18 Å^{-1} the agreement factors before inclusion of the H atoms of the NH_3 group were 5.1 and 7.6%. After inclusion of these atoms, these agreement factors dropped very significantly to 4.3 and 6.0%. A final difference Fourier synthesis over the asymmetric unit showed no peaks of height greater than 1.0 e$^-$/Å^3 and, in particular, showed no significant features in the vicinity of the NH_3 group. The height of a typical C atom in this structure on earlier electron density maps was 5.5 e$^-$/Å^3. Thus there is no evidence for additional atoms in the structure and the present diffraction evidence is strongly in favor of the formulation of the compound as $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. Additional chemical evidence for this formulation will be presented separately.[8]

An inspection of the data suggested that no correction for secondary extinction was necessary. Moreover, a comparison of $|F_o|$ *vs.* $|F_c|$ for various classes of observations based on $|F_o|$, Miller indices, and the scatter-

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

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[13] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

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

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

[16] J. M. Bijvoet and J. A. A. Ketelaar, *J. Am. Chem. Soc.*, **54**, 625 (1932).

TABLE I

FINAL LEAST-SQUARES PARAMETERS FOR $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

Atom	x	y	z	b_{11}[a]	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Os	$^1/_4$	0.08105 (4)[b]	0	0.00106 (1)	0.00587 (7)	0.00174 (2)	0	0.00027 (1)	0
Cl_1	$^1/_4$	−0.16688 (29)	0	0.00151 (7)	0.00622 (35)	0.00287 (13)	0	0.00045 (7)	0
Cl_2	0.19490 (9)	0.10405 (23)	0.11023 (13)	0.00155 (5)	0.01238 (32)	0.00282 (10)	0.00033 (10)	0.00074 (6)	−0.00149 (14)
P	0.15795 (9)	0.08244 (21)	−0.11250 (12)	0.00113 (5)	0.00625 (25)	0.00177 (9)	−0.00007 (9)	0.00033 (5)	0.00018 (12)
N	$^1/_4$	0.30541 (93)	0	0.00161 (24)	0.00710 (123)	0.00415 (54)	0	−0.00062 (28)	0

Group	x_c[c]	y_c	z_c	δ	ϵ	η	B_1	B_2	B_3	B_4	B_5	B_6
Ph_1	0.04043 (15)	−0.09365 (36)	−0.08659 (21)	−2.150 (5)	−2.226 (3)	−2.645 (5)	2.0 (1)	3.8 (2)	4.7 (2)	3.7 (2)	3.1 (2)	2.8 (2)
Ph_2	0.16117 (15)	−0.04228 (36)	−0.30134 (22)	−2.717 (4)	−2.766 (3)	1.745 (4)	1.9 (1)	3.3 (2)	3.8 (2)	3.6 (2)	4.4 (2)	3.8 (2)
Ph_3	0.11524 (16)	0.40543 (38)	−0.14074 (23)	−1.356 (3)	2.475 (4)	0.031 (4)	2.2 (1)	3.3 (2)	4.4 (2)	4.7 (2)	4.0 (2)	3.2 (2)

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [c] The angles δ, ϵ, and η (in radians) which bring about alignment of an internal coordinate system within the group with a fixed external system have been defined in previous papers: see R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). B_i is the isotropic thermal parameter (in Å^2) of atom i. The rings are numbered such that atom 1 is attached to P.

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS IN $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

Atom	x	y	z
		Ph_1	
C_1	0.0911 (2)[a]	−0.0165 (8)	−0.0962 (3)
C_2	0.0377 (3)	−0.0129 (5)	−0.1604 (2)
C_3	−0.0130 (2)	−0.0900 (8)	−0.1508 (3)
C_4	−0.0103 (2)	−0.1708 (9)	−0.0770 (3)
C_5	0.0432 (3)	−0.1745 (5)	−0.0128 (3)
C_6	0.0939 (2)	−0.0973 (7)	−0.0224 (3)
		Ph_2	
C_1	0.1617 (3)	0.0162 (5)	−0.2208 (2)
C_2	0.1404 (3)	0.0942 (4)	−0.2956 (3)
C_3	0.1398 (2)	0.0357 (5)	−0.3761 (2)
C_4	0.1606 (3)	−0.1008 (5)	−0.3819 (3)
C_5	0.1820 (3)	−0.1788 (4)	−0.3071 (3)
C_6	0.1825 (2)	−0.1203 (5)	−0.2266 (3)
		Ph_3	
C_1	0.1300 (3)	0.2634 (4)	−0.1340 (4)
C_2	0.0803 (2)	0.3132 (5)	−0.1037 (4)
C_3	0.0656 (2)	0.4552 (5)	−0.1104 (4)
C_4	0.1005 (3)	0.5474 (4)	−0.1475 (4)
C_5	0.1502 (3)	0.4977 (5)	−0.1778 (4)
C_6	0.1649 (2)	0.3557 (5)	−0.1711 (4)

[a] The estimated standard deviations here are derived from those of the group parameters and are meant to be used in error analyses on inter-ring distances. Intra-ring distances are, of course, fixed (C–C = 1.390 Å).

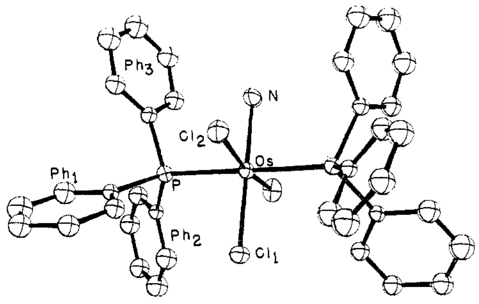

Figure 1.—A perspective drawing of a molecule of $OsCl_3(NH_3)(P(C_6H_5)_3)_2$, with H atoms omitted for clarity. There is a twofold symmetry axis through Cl_1–Os–N which relates the left half of the molecule to the right half.

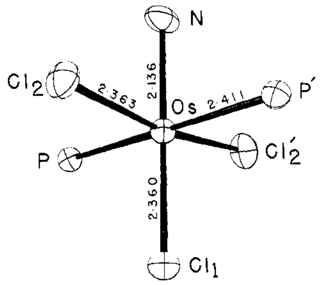

Figure 2.—A perspective view of the inner coordination about Os in $OsCl_3(NH_3)(P(C_6H_5)_3)_2$, showing principal bond distances.

ing angle showed no unexpected trends. Thus the relative weighting scheme is a reasonable one. The absolute weights are probably too large by a factor of 2 as the final value of the estimated standard deviation of an observation of unit weight is 2.06 e$^-$.

The final least-squares parameters are given in Table I, and Table II gives the coordinates of the group carbon atoms that may be derived from the data of Table I. The final values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table III.

Results and Discussion

The crystal structure, as defined by the unit cell dimensions, symmetry operations of space group I2/a, and the parameters of Table I, consists of loosely packed, monomeric units of $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. In Figure 1 the over-all molecular structure is displayed, and in Figure 2 only the inner coordination about the Os atom is shown. Principal intramolecular distances and angles and their standard deviations are given in Table IV. The root-mean-square amplitudes along the principal axes of thermal motion for the atoms that were refined anisotropically are shown in Table V. The directions of principal axes can be discerned, at least approximately, from the figures. Application of "corrections" to the bond lengths[17] to allow for the effects of thermal motion on the apparent positions of the atoms affects very little the differences among the bond lengths.

The packing is largely dictated by intermolecular contacts between the bulky phosphine ligands. This can be seen by comparing this structure with that of $ReNCl_2(P(C_6H_5)_3)_2$,[2] which crystallizes in the same space group, I2/a, with very similar cell dimensions: $OsCl_3(NH_3)(P(C_6H_5)_3)_2$, a = 22.43, b = 9.52, c =

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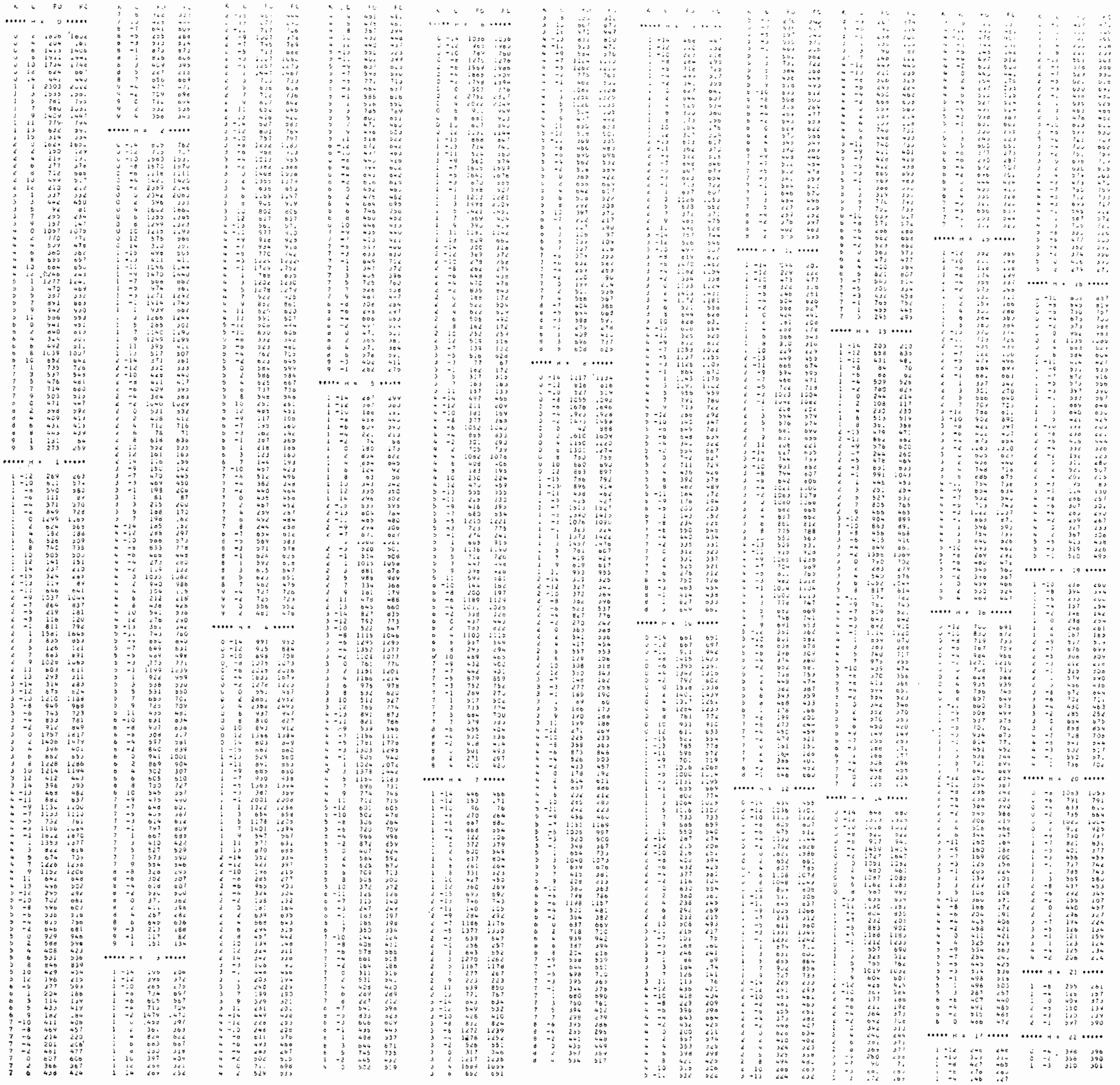
[17] W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR $OsCl_3(NH_3)(P(C_6H_5)_3)_2$



15.85 Å, β = 102° 51′; $ReNCl_2(P(C_6H_5)_3)_2$, a = 22.17, b = 9.53, c = 15.71 Å, β = 103° 26′. The orientations of the phenyl rings in the two compounds are only slightly different, and the volumes per triphenylphosphine group, 404 Å^3 for the rhenium compound and 412 Å^3 for the osmium compound, are only about 15% greater than that for triphenylphosphine itself.[18]

We have been unable to find structural information on other six-coordinate ammine complexes of a third-row transition metal. Thus direct comparisons with the present Os–NH_3 distance are not possible. The Os–NH_3 distance of 2.136 (9) Å does compare well with the Co–N distance of 2.144 (9) Å in $Co(NH_3)_6Cl_2$.[19] As expected, it is somewhat longer than the Pt–NH_3 distances of 2.01–2.06 Å in the four-coordinate, diamagnetic complexes $PtCl_2(C_2H_4)(NH(CH_3)_2)$,[20] $[Pt(NH_3)_4][PtCl_4]$,[21] and *cis*- and *trans*-$PtCl_2(NH_3)_2$.[22]

From our point of view, the most interesting compounds with which to compare the present structure are the rhenium imino complexes, and the important distances and angles in the present structure and the rhenium imino complexes are drawn up in Table VI. The points to note in this table are (1) on increasing the metal–nitrogen distance by 0.4 Å the remaining metal–ligand bond lengths decrease by 0.04–0.07 Å, (2) in the imino complexes the Cl(*trans*)–Re–ligand(*cis*) angles are all consistently considerably less than 90°, while the

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[18] J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

[19] M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

[20] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, **13**, 149 (1960).

[21] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Am. Chem. Soc.*, **79**, 3017 (1957).

[22] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc., A* 1609 (1966).

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

Os–N	2.136 (9)	Cl_1–Os–N	180
Os–Cl_1	2.360 (3)	Cl_1–Os–Cl_2	95.32 (5)
Os–Cl_2	2.363 (2)	Cl_1–Os–P	90.31 (5)
Os–P	2.411 (2)	Cl_2–Os–N	84.68 (5)
Cl_1–N	4.496 (10)	Cl_2–Os–P	92.52 (7)
Cl_1–Cl_2	3.491 (3)	Cl_2–Os–Cl_2'[a]	169.37 (11)
Cl_1–P	3.383 (3)	Cl_2–Os–P′	87.42 (7)
Cl_2–N	3.035 (6)	P–Os–N	89.69 (5)
Cl_2–P	3.449 (3)	P–Os–P′	179.37 (9)
Cl_2–P′	3.299 (3)	Os–P–Ph_1C_1	119.01 (37)[b]
Cl_2–Cl_2'	4.706 (4)	Os–P–Ph_2C_1	118.50 (31)[b]
P–N	3.212 (6)	Os–P–Ph_3C_1	110.08 (29)[b]
P–P′	4.821 (4)	Ph_1C_1–P–Ph_2C_1	99.38 (45)[b]
P–Ph_1C_1	1.836 (14)[b]	Ph_1C_1–P–Ph_3C_1	104.53 (40)[b]
P–Ph_2C_1	1.849 (10)[b]	Ph_2C_1–P–Ph_3C_1	103.36 (38)[b]
P–Ph_3C_1	1.839 (10)[b]		

[a] Atoms marked by a prime are related to the unprimed atom by a rotation around the twofold axis at $^1/_4, y, 0$. [b] These standard deviations were not calculated from the elements of the full variance–covariance matrix but were estimated by the methods of D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

TABLE V

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL AXES OF THERMAL VIBRATION IN $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

Atom	Min	Intermed	Max
Os	0.1451 (10)	0.1613 (9)	0.1641 (9)
Cl_1	0.169 (5)	0.186 (4)	0.192 (4)
Cl_2	0.157 (4)	0.199 (3)	0.249 (3)
P	0.145 (4)	0.165 (3)	0.171 (3)
N	0.165 (16)	0.181 (16)	0.268 (14)

Cl(*trans*)–Os–ligand(*cis*) angles are 90 and 95°, and (3) the nonbonded distances between adjacent atoms are very similar in all four compounds.

TABLE VI

COMPARISON OF THE INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN (A) $OsCl_3(NH_3)(P(C_6H_5)_3)_2$ WITH THOSE IN (B) $ReCl_3(NC_6H_4OCH_3)(P(C_2H_5)_2C_6H_5)_2$, (C) $ReCl_3(NC_6H_4COCH_3)(P(C_2H_5)_2C_6H_5)_2$, AND (D) $ReCl_3(NCH_3)(P(C_6H_5)_2C_2H_5)_2$

	A	B	C	D
	Distance			
M[a]–N	2.14	1.71	1.69	1.69
M–Cl(*trans*)[b]	2.36	2.43	2.41	2.41
M–Cl(*cis*)	2.36	2.42	2.40 2.43	2.41 2.43
M–P	2.41	2.47	2.46 2.46	2.48 2.49
Cl(*cis*)···N	3.04	3.04	2.98 3.11	2.94 3.11
P···N	3.21	3.15	3.02 3.15	3.12 3.12
Cl(*cis*)···Cl(*trans*)	3.49	3.34	3.28 3.30	3.28 3.34
P···Cl(*trans*)	3.38	3.28	3.32 3.32	3.26 3.37
P···Cl(*cis*)	3.30 3.45	3.42 3.48	3.36 3.41 3.42 3.56	3.30 3.42 3.47 3.63
	Angle			
Cl(*trans*)–M–Cl(*cis*)	95	87	87 85	88 85
Cl(*trans*)–M–P	90	84	86 86	84 87
Cl(*trans*)–M–N	180	180	175	175

[a] M refers to the central metal atom, Os or Re. [b] *cis* and *trans* are used here to denote positions relative to the N atom. All phosphorus atoms are *cis*.

All of these points lend further support to our previous suggestion[5] that the molecular configurations of the imino complexes are largely determined by intramolecular packing. Both the present complex and the imino complexes contain the $MCl_2(PR_3)_2$ moiety *cis* to the N atom. This unit is too overcrowded to be planar. In the osmium complex the overcrowding is relieved by a movement of the chlorine atoms out of the *cis* plane toward the N atom until the Cl···N distance is at its optimum value, about 3.0 Å. In the imino complexes, because of the short, strong metal–nitrogen multiple bond, the N atom is already too close to the *cis* ligands for this to happen, and all of the *cis* ligands must move away from the N atom to achieve reasonable N···*cis*-ligand distances. However, moving all of the *cis* ligands away from the N atom simply results in even closer packing of the *cis* ligands, and to relieve this the rhenium–*cis*-ligand bonds must lengthen. Hence, we find longer *cis* bonds in the imino complexes than in the ammine complex as well as a different type of distortion from an ideal octahedral configuration about the metal.

Acknowledgment.—We have benefited greatly from close collaboration with Professor J. Chatt. We thank the National Science Foundation for its support of this work.