

## Studies of Metal-Nitrogen Multiple Bonds. III. The Crystal and Molecular Structures of Trichloro(*p*-methoxyphenylimino)bis(diethylphenylphosphine)rhenium(V) and Trichloro(*p*-acetylphenylimino)bis(diethylphenylphosphine)rhenium(V)

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The crystal and molecular structures of two arylimino complexes of rhenium(V)—trichloro(*p*-methoxyphenylimino)bis(diethylphenylphosphine)rhenium(V),  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ , and trichloro(*p*-acetylphenylimino)bis(diethylphenylphosphine)rhenium(V),  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ —have each been determined from three-dimensional X-ray data collected by counter methods. The structure of the methoxy compound has been refined by least-squares techniques to a final *R* factor on *F* of 2.7% for the 2952 independent reflections above background. The material crystallizes in space group  $\text{C}_{2h}^2\text{-C2/c}$  of the monoclinic system in a cell of dimensions  $a = 15.427$  (6) Å,  $b = 13.998$  (6) Å,  $c = 17.062$  (7) Å,  $\beta = 126.55$  (2)°. The density of  $1.60 \text{ g/cm}^3$  calculated for four formula units in the cell agrees well with the observed density of  $1.61 \pm 0.01 \text{ g/cm}^3$ . The well-separated individual molecules are required crystallographically to possess  $\text{C}_2$  symmetry. The over-all structure around Re is octahedral with P atoms *trans* to one another and Cl atoms *trans* to one another in the basal plane and the third Cl at the one vertex and the arylimino group (coordinated to Re *via* the N atom) at the other. Neither the Re-N-C angle nor the C-O-CH<sub>3</sub> angle is 180° and so the imposition of  $\text{C}_2$  symmetry on the molecule requires that the  $\text{C}_6\text{H}_4\text{-O-CH}_3$  portion of the molecule be disordered. The Re-Cl distance in the equatorial plane is 2.421 (1) Å while the Re-Cl distance *trans* to the N ligand is 2.432 (2) Å. The Re-P distance is 2.470 (1) Å. The acetyl compound has been refined by least-squares techniques to give a final *R* factor of 3.0% on *F* for the 3027 independent reflections above background. The compound crystallizes in the monoclinic space group  $\text{C}_{2h}^2\text{-P2}_1\text{/c}$ . The cell dimensions are  $a = 10.52$  (2) Å,  $b = 16.06$  (3) Å,  $c = 18.15$  (3) Å,  $\beta = 91.65$  (5)°. The calculated density for four molecules per unit cell is  $1.64 \text{ g/cm}^3$ ; the observed density was  $1.63 \pm 0.01 \text{ g/cm}^3$ . No crystallographic symmetry is imposed on the molecule. The over-all molecular structure is the same as that found for the methoxy compound. The Re-Cl distance *trans* to the N atom is 2.410 (3) Å and the *cis* distances are 2.433 (3) and 2.399 (3) Å. The Re-P distances are 2.457 (4) and 2.461 (4) Å. The octahedral configurations in both complexes are slightly distorted: the atoms in the equatorial plane are bent toward the axial Cl atom. The Re-N distances in the methoxy and acetyl complexes are 1.709 (4) and 1.690 (5) Å, respectively. Both of these bonds are significantly shorter than the value 1.788 (11) Å found previously in  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ . Hence, formal double bonds in the arylimino complexes are shorter than the formal triple bond in the related nitrido complex.

### Introduction

A number of arylimino and nitrido complexes of rhenium(V) have been prepared and characterized by Chatt, *et al.*<sup>1</sup> The structures of two nitrido complexes,  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$  and  $\text{ReNCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ , have been reported<sup>2,3</sup> in the first two papers in this series. The Re-N distances in these two compounds are 1.788 (11) and 1.603 (9) Å, respectively.

The arylimino complexes of rhenium(V) are of unusual interest for they appear to be the only known examples in transition metal chemistry where the arylimino group is a ligand. These complexes are closely related to the nitrido complexes of rhenium(V), and so their structures are of interest for comparison with the structures of the corresponding nitrido complexes. Specifically, the arylimino complexes  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{X})(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$  (where X is a group *para* to N) form an interesting structural series since their dipole moments appear to be a function of the mesomeric properties of the group X. As the electron-releasing properties of X increase, the dipole moments of

the compounds also increase. Presumably an electron-releasing group *para* to the nitrogen will cause a drift of electrons toward the nitrogen which should affect the interaction of the nitrogen lone-pair electrons with the d orbitals on the rhenium atom. Thus the group X should exert an effect on the Re-N bond. If sufficient care is taken in the structure determinations, it should be possible to assess this effect.

This paper reports the precise structures of two arylimino complexes, one from each end of the dipole moment range reported by Chatt, *et al.*<sup>1</sup> The first ( $\mu = 7.2 \text{ D}$ ) contains the strongly electron-releasing methoxy group ( $\text{X} = \text{OCH}_3$ ), and the second ( $\mu = 4.5 \text{ D}$ ) contains the strongly electron-withdrawing acetyl group ( $\text{X} = \text{COCH}_3$ ). Although we had anticipated that information from these studies would increase our understanding of metal-nitrogen multiple bonds in general and of rhenium-nitrogen multiple bonds in particular, it has, for the time being, left us with more unexplained effects than we had hoped.

### Collection and Reduction of the Intensity Data

Crystals of trichloro(*p*-methoxyphenylimino)bis(diethylphenylphosphine)rhenium(V) were prepared by Miss R. J. Paske and kindly supplied by Professor J. Chatt; crystals of trichloro(*p*-acetylphenylimino)bis(diethylphenylphosphine)rhenium(V) were prepared

(1) J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1012 (1964). These authors used the nomenclature "arylimido," but we adopt "arylimino" in accordance with the conventions of *Chemical Abstracts*.

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

(3) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

by the method of Chatt, *et al.*<sup>1</sup> Preliminary optical and X-ray examinations showed that both compounds crystallize in the monoclinic system.

The cell constants and their standard deviations for each compound were obtained from a least-squares refinement<sup>2</sup> of the setting angles of a number of reflections that had been carefully centered on a Picker automatic X-ray diffractometer at 22°. The results were: methoxy compound (28 reflections, Cu K $\alpha_1$  radiation,  $\lambda$  1.54056 Å),  $a = 15.427$  (6) Å,  $b = 13.998$  (6) Å,  $c = 17.062$  (7) Å,  $\cos \beta = -0.5955$  (2); acetyl compound (13 reflections, Mo K $\alpha_1$  radiation,  $\lambda$  0.70930 Å),  $a = 10.52$  (2) Å,  $b = 16.06$  (3) Å,  $c = 18.15$  (3) Å,  $\cos \beta = -0.0289$  (4).

The systematic extinctions observed on Weissenberg and precession photographs of the methoxy compound are:  $hkl$  for  $h + k$  odd and  $h0l$  for  $l$  odd (and for  $h$  odd). These extinctions are consistent with either of the space groups C<sub>s</sub><sup>4</sup>-Cc or C<sub>2h</sub><sup>6</sup>-C2/c. The calculated density of the methoxy compound, assuming four molecules per unit cell, is 1.60 g/cm<sup>3</sup>. This agrees well with the density 1.61  $\pm$  0.01 g/cm<sup>3</sup> observed by flotation of the crystals in aqueous potassium iodide. If the space group is C2/c, then the molecule is required to possess twofold symmetry.

The systematic extinctions observed for the acetyl compound are  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd. These absences are consistent only with space group C<sub>2h</sub><sup>5</sup>-P2<sub>1</sub>/c. The observed density is 1.63  $\pm$  0.01 g/cm<sup>3</sup>, and the density calculated for four molecules per cell is 1.64 g/cm<sup>3</sup>. Thus no symmetry need be imposed on the molecule.

The experimental and computational procedures used in the data collection were the same for each compound and parallel those described previously.<sup>2,3</sup>

A well-formed crystal of each compound was chosen, each with a maximum dimension of  $\approx 0.5$  mm. In preparation for absorption corrections each crystal was carefully measured using a micrometer eyepiece, and the crystal faces were identified by means of an optical goniometer. For the methoxy compound the following forms were developed: {100}, {001}, {11 $\bar{1}$ }, and {11 $\bar{2}$ }. The approximate dimensions of the crystal were 0.2  $\times$  0.2  $\times$  0.5 mm. For the acetyl compound the following forms were developed: {100}, {110}, and {012}. The approximate dimensions of the crystal were 0.1  $\times$  0.4  $\times$  0.5 mm.

The methoxy crystal was mounted on the diffractometer with the  $a^*$  direction within 10° of the spindle axis; the acetyl compound was mounted with  $c^*$  within 10° of the spindle axis.

$\omega$  scans through several reflections showed that crystal mosaicity was reasonably low for each compound.

For the collection of both data sets, Mo K $\alpha$  radiation ( $\lambda$  0.7107 Å) was used, and the diffracted beams were filtered through 4.5 mils of Zr foil. The intensities were measured by the  $\theta$ - $2\theta$  scan technique at a take-off angle of 1.2°. At this angle the intensity of a reflection was approximately 80% of its maximum value as a function of take-off angle. The crystal-to-

counter distance was 35 cm. Since the stronger peaks had visible tails to higher  $2\theta$  a nonsymmetric scan range of  $-0.50$  to  $+0.75^\circ$  in  $2\theta$  was used. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The scan rate was 1°/min. The Picker machine system automatically inserts attenuators into the diffracted beam if its intensity exceeds about 7000 counts/sec during the scan. The thickness of the copper foil attenuators was chosen to give attenuator factors of approximately 2.5. Thus errors due to coincidence losses were minimized.

Intensity data for the methoxy compound were collected from the  $hkl$  planes out to  $\theta(\text{Mo K}\alpha) \leq 27.5^\circ$ , and data out to the same angle in the remaining planes  $h\bar{k}l$ ,  $\bar{h}kl$ , and  $\bar{h}\bar{k}l$  of the monoclinic form were also collected where the corresponding reflection in the  $hkl$  set had been found to have  $I > 3\sigma(I)$ . A total of 12,625 reflections were measured.

Intensity data for the acetyl complex were collected only from the  $hkl$  planes out to  $\theta(\text{Mo K}\alpha) \leq 21.5^\circ$ . A total of 3442 reflections were measured.

The percentage of intensities above background decreases rapidly with scattering angle. In the present cases additional intensity data could have been collected at higher angles, but the present data sets are sufficient to define both structures to high precision.

The data for each compound were processed in the manner described previously.<sup>2</sup> After initial correction for background, the standard deviation,  $\sigma(I)$ , of the corrected intensity,  $I$ , was estimated 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 count obtained in time  $t_c$ ,  $B_1$  and  $B_2$  are the background counts each obtained in time  $t_b$ , and  $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$ . The values of  $p$  for the acetyl and methoxy compounds were taken as 0.035 and 0.030, respectively.

The intensities were next corrected for Lorentz-polarization factors and then for absorption. The calculated absorption coefficient for the methoxy compound is 47.42 cm<sup>-1</sup> and the transmission factors ranged from 0.43 to 0.50. The calculated absorption coefficient for the acetyl compound is 45.72 cm<sup>-1</sup> and the transmission factors ranged from 0.33 to 0.67.

Since it had been found (see next section) that the space group of the methoxy compound is C2/c rather than Cc, the four equivalent sets of data were averaged together to give a total of 3404 independent reflections. Of these intensity values, 452 were less than three times their standard deviations. These reflections will be referred to as being below background.

Of the 3442 independent reflections measured for the acetyl compound, 3027 were found to be above background.

#### Choice of Space Group for the Methoxy Compound

The anomalous scattering of X-rays can be used to resolve space group ambiguities. The anomalous scattering of Mo K $\alpha$  radiation by Re (and even by Cl

and P) is highly significant at the level of precision with which intensity data can be obtained by counter methods. If the material crystallizes in the noncentrosymmetric space group Cc, then it can be shown<sup>4</sup> that  $F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l})$  and that  $F^2(\bar{h}\bar{k}l) = F^2(hk\bar{l})$ , but that because of the anomalous scattering  $F^2(hkl) \neq F^2(\bar{h}\bar{k}\bar{l})$ . Thus we would expect the four equivalent sets of the methoxy compound to break up into two nonequivalent sets if the space group is Cc. If the space group is the centrosymmetric one, C2/c, all four sets should remain equivalent. A careful search of the full sphere of data on the methoxy compound revealed no systematic variation in intensity among the four sets of data. This provides strong evidence that the space group is indeed the centrosymmetric one, C2/c.

Additional evidence that supports or at least does not contradict this conclusion includes (1) the absence of a detectable piezoelectric effect and (2) the fact that the point symmetry of all of the well-formed crystals of the compound was 2/m.

Accordingly it was assumed that the space group is C2/c, even though such an assumption imposes C<sub>2</sub> symmetry on the molecule. C<sub>2</sub> symmetry is possible for the ReNCl<sub>3</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> portion of the molecule; yet, since one does not expect the bond angle at N to be 180° and since the bond angle at O is surely not 180°, the imposition of C<sub>2</sub> symmetry on the molecule requires that some or all of the C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> portion of the molecule be disordered about the C<sub>2</sub> axis. This assumption has been justified by the final results of the analysis.

#### Solution and Refinement of the Structures

In the least-squares refinements the function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and  $w$  is  $1/\sigma^2(F_o)$ . The standard deviation of  $F_o$ ,  $\sigma(F_o)$ , was taken as  $\sigma(F_o^2)/2F_o$ . The residuals  $R_1$  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, N, O, and C were those tabulated by Ibers<sup>5</sup> and those for Re were calculated by Cromer and Waber.<sup>6</sup> The hydrogen-scattering factors were those of Stewart, *et al.*<sup>7</sup>

The effects of anomalous scattering were included in the structure-factor calculations;<sup>8</sup> the values of  $\Delta f'$  and  $\Delta f''$  for Re, P, and Cl were those given by Cromer.<sup>9</sup>

The course of the refinement for each compound is shown in Table I. In each case the Re atom was easily located from inspection of the three-dimensional Patterson function,<sup>10</sup> and the remaining nonhydrogen atoms were found from successive Fourier syntheses

TABLE I  
COURSE OF REFINEMENT

Atoms included	—Methoxy—		—Acetyl—	
	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>
Re	37.6	48.4	35.9	43.8
All nonhydrogen atoms (all isotropic)	6.5	8.0	6.0	7.5
Re, N, Cl, P anisotropic	3.4	4.4	3.5	4.3
Extinction included	3.2	4.2		
All nongroup atoms anisotropic	2.9	4.0	Not applicable	
Hydrogen included	2.7	3.3	3.0	3.8

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES OF THE FORM {532} FOR THE ORDERED AND DISORDERED MODELS

hkl	F <sub>o</sub>	F <sub>c</sub>   (Cc)	F <sub>c</sub>   (C2/c, disordered)
532	11.4 (5)	2.5	11.3
532	12.6 (5)	2.5	11.3
532	12.3 (5)	24.6	11.3
532	12.9 (4)	24.6	11.3

and least-squares refinements. For the methoxy compound the atomic positions supported the proposition that the ReNCl<sub>3</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> group has crystallographic twofold symmetry. In accordance with this, the structure was refined in space group C2/c with two half-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> groups related by the C<sub>2</sub> axis.

The independent phenyl rings as well as the C<sub>6</sub>H<sub>4</sub> portion of the NC<sub>6</sub>H<sub>4</sub>X groups were refined as planar rigid groups (D<sub>6h</sub> symmetry, with C—C = 1.392 Å) in the manner described previously.<sup>11</sup>

For the methoxy compound the low-order strong reflections were found to have  $F_o$  consistently less than  $F_c$ , indicative of extinction effects. To handle this, Zachariasen's<sup>12</sup> latest formulation of the extinction problem was adopted, and his extinction parameter was refined as a variable in the least-squares analysis.<sup>13</sup> The resultant value of Zachariasen's parameter,  $C$ , was  $2.9(4) \times 10^{-7}$  for intensities on an absolute scale. This resulted in a considerable improvement of the agreement for the low-order strong reflections. The correction was a small one, and so the assumptions implicit in this procedure, namely, that the mosaicity of the crystal is isotropic and that the crystal is spherical in shape, are not drastic ones. It should be emphasized that this procedure of refining an extinction parameter is far more desirable than the arbitrary elimination of certain reflections from the analysis. There was no evidence of extinction effects for the acetyl compound.

The structures were refined to convergence with all nonhydrogen nongroup atoms anisotropic in the methoxy structure and, owing to computer limitations, only the Re, P, Cl, and N atoms anisotropic in the acetyl structure. All other nonhydrogen atoms were refined isotropically. At this point, difference Fourier maps were calculated using only the planes for which  $\lambda^{-1} \sin \theta$  was less than  $0.35 \text{ \AA}^{-1}$  in order to improve the resolution of missing hydrogen atoms.<sup>11</sup> Both maps showed a disturbance around the Re atom, but the map from the methoxy data was dominated by peaks of

(4) J. A. Ibers, *Acta Cryst.*, **22**, 604 (1967).

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

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

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

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

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

(10) The programs used in this work were PICK and PICKOUT, for generating and processing the data, NUGLS, the group-refinement program, and local modifications of Hamilton's GONO9 absorption correction program, Zalkin's FORDAP Fourier program, the Busing-Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

(11) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

(12) W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

(13) R. G. Delaplane and J. A. Ibers, unpublished work.

TABLE IIIa

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (ELECTRONS X 5) FOR  $ReCl_5(NC_6H_5)_2(P(C_2H_5)_2C_6H_5)_2$

Table with columns for observed and calculated amplitudes (K, L, F, O, FC) and corresponding values for various reflections. The table is organized into multiple sections with different reflection indices.

TABLE IIIa (Continued)

K	L	Fo	Fc	K	L	Fo	Fc	K	L	Fo	Fc	K	L	Fo	Fc	K	L	Fo	Fc
11	-12	88	107	-4	19	166	164	8	-4	313	320	3	-12	176	168	0	-13	282	492

about  $0.5 e^{-}/\text{\AA}^3$  in the positions where hydrogen atoms were expected. In the map from the acetyl data there was density in the regions where hydrogen peaks were expected, but it was not possible to resolve individual peaks. This is in accord with the experience of Zalkin, Hopkins, and Templeton,<sup>14</sup> who also found that to locate hydrogens attached to carbon it is first necessary to remove the anisotropy of the carbon atom.

The phenyl and methylene hydrogens were put into the structures in accordance with the electron density maps and with the well-known stereochemistry of such groups. The methyl hydrogens in the methoxy structure were put in at the positions calculated for the best fit of ideal trigonal groups to the observed peaks. For each of the independent ethyl groups in the methoxy compound the best fit was found to occur when the methyl hydrogens were staggered with respect to the methylene hydrogens. For the acetyl compound the methyl hydrogens in the four ethyl groups were also put in as ideal groups staggered with respect to the methylene hydrogens and the methyl hydrogens of the acetyl grouping were included in positions consistent with both the crystal packing and the observed electron density.

The actual location of the hydrogen atoms in the methoxy structure gives further support for the disordered model. If the grouping  $\text{ReNCl}_3(\text{P}(\text{C}_2\text{H}_5)_2)_2\text{C}_6\text{H}_5$  did not have precise  $C_2$  symmetry, it is very unlikely that the hydrogens would have been visible.

It is well known that light atom-hydrogen atom distances determined by X-ray diffraction are abnormally short when compared with spectroscopic values. Thus C-H distances of  $0.75\text{--}0.9 \text{ \AA}$  are not uncommonly found. Although the reasons for this shortening are the subject of some discussion,<sup>16</sup> the immediate question at hand is whether or not it is better to fix the C-H distances in this structure at  $0.9 \text{ \AA}$  or at the spectro-

scopic value of  $1.1 \text{ \AA}$ . Ordinarily this question would not arise in structures containing rhenium as well as hydrogen, but the quality of the present data appears to be exceptionally high. The temperature factors for all hydrogen atoms were fixed at  $5 \text{ \AA}^2$ . Structure factor calculations indicated that a C-H distance of  $0.9 \text{ \AA}$  gives a better fit than a C-H distance of  $1.1 \text{ \AA}$ . This suggests that the actual location of the hydrogen atom positions in this structure is reliable to  $0.1 \text{ \AA}$  or less and that, whatever the reasons for the abnormally short C-H distances found in X-ray diffraction studies of light atom-hydrogen atom structures, they apply here as well. The error of an observation of unit weight was 1.33 for the theoretical value of 1.0 to suggest that the absolute weighting scheme is a reasonable one. An analysis of the  $R_1$  and  $R_2$  factors as a function of  $F_o$ , scattering angle, and Miller indices showed no unexpected trends and suggests that the relative weighting scheme is also reasonable. Moreover, the final value of  $R_2$ , based on  $F^2$ , is  $6.6\%$ , and this compares reasonably well with that of  $5.2\%$  predicted from the agreement between the theoretical value of 1.0 and the observed value of 1.33. The fact that these two values do not agree exactly suggests that some small systematic errors remain in the data set or in the model. Among the latter may be the assumption that the phenyl rings have C-C distances of  $1.392 \text{ \AA}$ . This is the equilibrium distance. Since the rings are undergoing motion in the solid, the distance derived from the experiment would be somewhat shorter, perhaps  $1.38 \text{ \AA}$ . In the absence of a better description of the rigid-body motions of these rings, it is probably desirable to assume a slightly foreshortened C-C distance.

The error of an observation of unit weight is 1.59 for the acetyl compound. Because only an independent set of reflections was collected for this substance, the assignment of reliable weights, especially on an absolute

(14) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

(15) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

TABLE IIIb  
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (ELECTRONS X 10) FOR ReCl5(NC4H4COCH3)3(P(C2H5)2C6H5)2

Table with multiple columns of numerical data representing observed and calculated structure amplitudes. The columns are organized into groups labeled with 'K L FO FC' and 'K L FO FC' for various reflections. The data includes observed values and calculated values for each reflection, with some reflections marked as 'OBSERVED' or 'CALCULATED'. The table is very dense and spans the entire page.



TABLE IV  
 FINAL LEAST-SQUARES PARAMETERS
(a)  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ .

Atom	$x$	$y$	$z$	$B_{11}^a$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$			
Re	0	0.02204 (1) <sup>b</sup>	1/4	0.00413 (2)	0.00226 (1)	0.00391 (1)	0	0.00239 (1)	0			
Cl <sub>1</sub>	0	-0.15171 (10)	1/4	0.00695 (11)	0.00238 (6)	0.00682 (10)	0	0.00347 (10)	0			
Cl <sub>2</sub>	0.04583 (10)	-0.01249 (9)	0.13695 (8)	0.00565 (8)	0.00554 (6)	0.00517 (6)	-0.00009 (5)	0.00410 (6)	-0.00043 (5)			
P	-0.19339 (9)	0.00325 (7)	0.11448 (8)	0.00439 (6)	0.00306 (5)	0.00426 (6)	-0.00021 (4)	0.00239 (5)	-0.00022 (4)			
N	0	0.14410 (31)	1/4	0.00466 (31)	0.00282 (21)	0.00461 (27)	0	0.00288 (26)	0			
O	0.03317 (80)	0.53454 (47)	0.24998 (81)	0.01244 (101)	0.00279 (63)	0.01047 (53)	-0.00059 (39)	0.00576 (77)	0.00062 (42)			
Me <sup>c</sup>	-0.02840 (116)	0.59587 (77)	0.26574 (94)	0.01240 (141)	0.00343 (50)	0.00712 (84)	0.00107 (65)	0.00301 (68)	-0.00082 (55)			
Et <sub>1</sub> C <sub>1</sub>	-0.25814 (46)	-0.09547 (36)	0.13053 (36)	0.00532 (33)	0.00510 (26)	0.00584 (31)	-0.00169 (24)	0.00385 (29)	-0.00021 (24)			
Et <sub>1</sub> C <sub>2</sub>	-0.37910 (48)	-0.10426 (52)	0.05170 (42)	0.00700 (42)	0.00927 (45)	0.00636 (41)	-0.00305 (35)	0.00394 (37)	-0.00086 (35)			
Et <sub>2</sub> C <sub>1</sub>	-0.22623 (39)	-0.01458 (38)	-0.00688 (33)	0.00609 (32)	0.00456 (23)	0.00415 (23)	0.00004 (22)	0.00236 (24)	-0.00048 (19)			
Et <sub>2</sub> C <sub>2</sub>	-0.19467 (45)	-0.11299 (40)	-0.02085 (38)	0.00889 (45)	0.00553 (30)	0.00623 (32)	0.00007 (29)	0.00395 (34)	-0.00175 (25)			
Group	$x_c^d$	$y_c$	$z_c$	$\delta$	$\epsilon$	$\eta$	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$
Ph <sub>1</sub>	-0.32858 (18)	0.18738 (16)	0.09760 (16)	0.5222 (71)	1.8900 (17)	1.6012 (71)	3.46 (7)	3.98 (8)	4.93 (10)	5.47 (11)	5.94 (13)	5.17 (11)
PhN	0.01364 (50)	0.34117 (24)	0.25140 (52)	3.0891 (50)	3.1941 (55)	0.7239 (33)	2.72 (10)	4.41 (21)	4.77 (21)	3.40 (15)	3.98 (17)	3.89 (18)

(b)  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ .

Atom	$x$	$y$	$z$	$B(A^2)$ or		$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$			
				$B_{11}^a$	$B_{22}$							
Re	0.21119 (2) <sup>b</sup>	0.18152 (2)	0.16740 (1)	0.00542 (3)	0.00295 (2)	0.00226 (1)	0.00012 (1)	-0.00028 (1)	-0.00020 (1)			
Cl <sub>1</sub>	0.38606 (16)	0.12483 (11)	0.23996 (10)	0.00705 (18)	0.00423 (9)	0.00341 (7)	0.00065 (10)	-0.00144 (9)	-0.00018 (6)			
Cl <sub>2</sub>	0.11627 (17)	0.21468 (12)	0.28235 (10)	0.00825 (19)	0.00465 (9)	0.00287 (6)	-0.00041 (10)	0.00097 (9)	-0.00075 (6)			
Cl <sub>3</sub>	0.33544 (18)	0.14328 (12)	0.06162 (10)	0.00985 (21)	0.00431 (9)	0.00288 (7)	-0.00012 (11)	0.00099 (9)	-0.00074 (6)			
P <sub>1</sub>	0.11521 (16)	0.04263 (11)	0.17692 (9)	0.00572 (18)	0.00293 (7)	0.00253 (2)	0.00015 (9)	-0.00047 (8)	0.00002 (6)			
P <sub>2</sub>	0.32831 (17)	0.31408 (11)	0.17329 (10)	0.00656 (19)	0.00308 (8)	0.00301 (7)	-0.00040 (9)	0.00007 (9)	-0.00033 (6)			
N	0.09053 (48)	0.21447 (31)	0.11126 (28)	0.00706 (57)	0.00263 (22)	0.00243 (19)	-0.00059 (29)	-0.00033 (26)	-0.00028 (17)			
AcC <sup>c</sup>	-0.29450 (74)	0.28698 (49)	-0.10301 (44)	4.59 (16)								
AcO	-0.27351 (57)	0.27062 (36)	-0.16686 (33)	6.44 (13)								
AcMe	-0.41523 (99)	0.32115 (57)	-0.08167 (57)	7.25 (24)								
Et <sub>1</sub> C <sub>1</sub>	0.13141 (67)	-0.00384 (43)	0.26758 (37)	3.96 (14)								
Et <sub>1</sub> C <sub>2</sub>	0.07799 (80)	-0.09203 (51)	0.27333 (46)	5.63 (18)								
Et <sub>2</sub> C <sub>1</sub>	0.17152 (67)	-0.03466 (43)	0.11341 (38)	4.06 (14)								
Et <sub>2</sub> C <sub>2</sub>	0.30902 (78)	-0.06082 (50)	0.12730 (44)	5.19 (18)								
Et <sub>3</sub> C <sub>1</sub>	0.49647 (73)	0.30624 (44)	0.15601 (42)	4.49 (16)								
Et <sub>3</sub> C <sub>2</sub>	0.56537 (83)	0.38850 (54)	0.15064 (48)	6.03 (20)								
Et <sub>4</sub> C <sub>1</sub>	0.32008 (71)	0.37240 (45)	0.25882 (40)	4.33 (16)								
Et <sub>4</sub> C <sub>2</sub>	0.38864 (78)	0.33105 (47)	0.32361 (44)	5.02 (17)								
Group	$x_c^d$	$y_c$	$z_c$	$\delta$	$\epsilon$	$\eta$	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$
Ph <sub>1</sub>	-0.18695 (28)	0.05357 (17)	0.14692 (16)	-3.0063 (42)	2.1426 (28)	2.8883 (44)	2.91 (12)	3.69 (13)	4.04 (14)	4.23 (15)	4.66 (16)	4.23 (15)
Ph <sub>2</sub>	0.22240 (33)	0.43559 (22)	0.04551 (20)	0.5183 (50)	-2.3815 (29)	1.5633 (49)	3.80 (13)	5.61 (19)	6.73 (22)	7.14 (22)	6.40 (21)	5.47 (18)
PhN	-0.09938 (26)	0.24895 (16)	0.00681 (16)	-1.7420 (42)	2.2913 (21)	1.5031 (41)	2.80 (12)	3.28 (13)	3.99 (14)	3.36 (13)	4.17 (15)	4.07 (15)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is given by  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. <sup>c</sup> Et<sub>1</sub>C<sub>1</sub> is carbon atom 1 in ethyl group 1; similarly Ph<sub>2</sub>C<sub>1</sub> is the carbon atom in phenyl group 2 attached to P<sub>2</sub>. AcC, AcO, and AcMe are the C, O, and CH<sub>3</sub> of the acetyl group. PhN is the phenyl group attached to nitrogen. <sup>d</sup> The angles  $\delta$ ,  $\epsilon$ , and  $\eta$  in radians which bring about alignment (except for translation) of an internal coordinate system within the group with a fixed external coordinate system have been defined in previous papers. See ref 11 and R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).  $B_i$  is the isotropic thermal parameter of atom  $i$  in Å<sup>2</sup>. The rings are numbered such that C<sub>1</sub> is attached to P or N; C<sub>4</sub> is *para* to C<sub>1</sub>.

Cl<sub>1</sub>-Re-P and Cl<sub>1</sub>-Re-Cl<sub>2</sub> are 83.9 and 86.8°, respectively. In the acetyl compound both species of ligands are bent by almost the same amount so that all Cl<sub>1</sub>-Re-*cis*-ligand angles are within 1° of 86°. In addition the Cl<sub>1</sub>-Re-N angle in the acetyl compound is 175.0°. This angle in the methoxy compound is 180°. The N atom is bent toward the bisector of the P<sub>1</sub>-Re-Cl<sub>3</sub> angle such that the angles P<sub>1</sub>-Re-N and Cl<sub>3</sub>-Re-N are 91.4 and 90.8°, and the angles P<sub>2</sub>-Re-N and Cl<sub>2</sub>-Re-N are 97.5 and 97.0°. The P<sub>1</sub>-Re-Cl<sub>3</sub> angle is also rather

larger at 93.3° than the other three angles in the basal plane of the octahedron (87.6, 89.5, 88.5°). Presumably this is to make room for the N atom.

The variation of the dipole moments with the mesomeric properties of the *para* substituent suggests that there is considerable electron transfer across the aryl-imino ring. Such electron transfer might cause some distortion of the phenyl ring toward a quinoid structure. Unfortunately we refined the phenyl rings as rigid groups. Insufficient computer storage space prevented



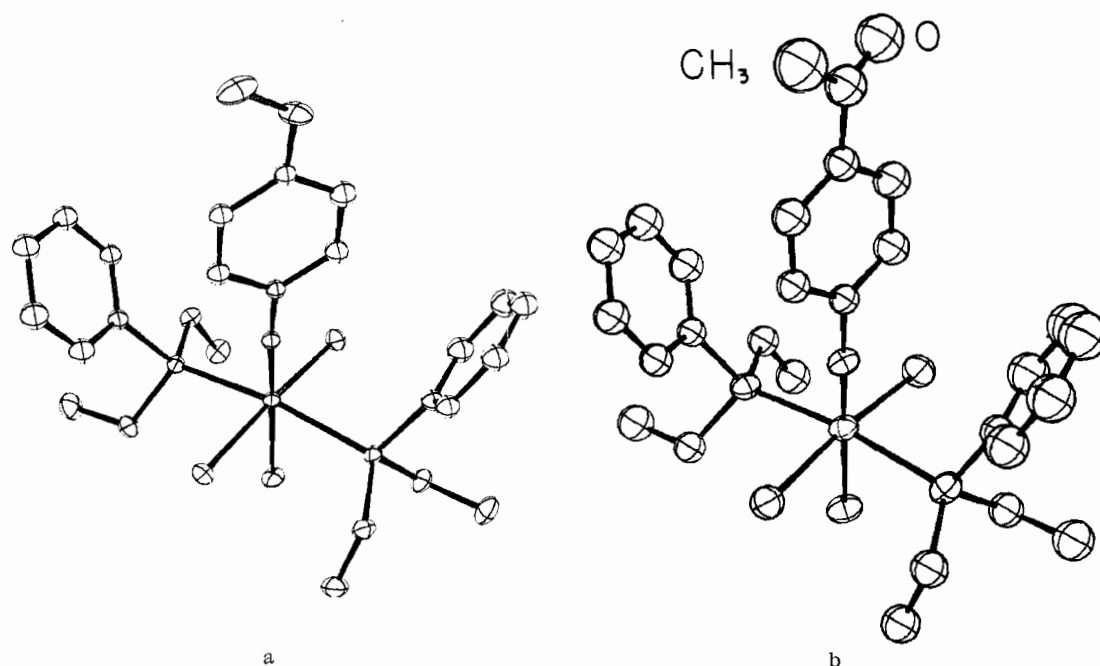


Figure 1.—Perspective drawings of the over-all molecular configuration of (a)  $\text{ReCl}_5(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$  and (b)  $\text{ReCl}_5(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ .

TABLE Va  
DERIVED PARAMETERS FOR GROUP CARBON ATOMS  
IN  $\text{ReCl}_5(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$

	<i>x</i>	<i>y</i>	<i>z</i>
Ph			
C <sub>1</sub>	-0.27253 (94) <sup>a</sup>	0.10701 (53)	0.10221 (54)
C <sub>2</sub>	-0.31575 (40)	0.17064 (28)	0.02458 (25)
C <sub>3</sub>	-0.37180 (64)	0.25101 (37)	0.01998 (38)
C <sub>4</sub>	-0.38463 (96)	0.26775 (54)	0.09300 (56)
C <sub>5</sub>	-0.34140 (44)	0.20413 (31)	0.17063 (29)
C <sub>6</sub>	-0.28535 (64)	0.12376 (38)	0.17523 (37)
PhN			
C <sub>1</sub>	0.00776 (91)	0.24190 (24)	0.25252 (93)
C <sub>2</sub>	0.08316 (74)	0.28515 (51)	0.24427 (78)
C <sub>3</sub>	0.08905 (49)	0.38442 (54)	0.24316 (54)
C <sub>4</sub>	0.01952 (55)	0.44044 (24)	0.25029 (52)
C <sub>5</sub>	-0.05589 (50)	0.39718 (48)	0.25853 (52)
C <sub>6</sub>	-0.06177 (69)	0.29792 (51)	0.25965 (74)

<sup>a</sup> The estimated standard deviations here and in Table Vb 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 = 1.392 Å).

us from refining any more parameters for the acetyl problem. The disorder of the  $\text{C}_6\text{H}_4\text{OCH}_3$  portion of the molecule in the methoxy compound presented another problem. In the disordered model, atom C<sub>1</sub> of PhN lies within 0.1 Å of the crystallographic twofold axis, and hence the electron density of this atom and its symmetry-related counterpart are not resolved. It would have been difficult to refine the position of this atom without the use of a rigid group (*cf.* the structure of azulene<sup>18</sup>). However, there is evidence that the quinoid character of the ring should be fairly small.

(18) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

TABLE Vb  
DERIVED PARAMETERS FOR GROUP CARBON ATOMS  
IN  $\text{ReCl}_5(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$

	<i>x</i>	<i>y</i>	<i>z</i>
Ph <sub>1</sub>			
C <sub>1</sub>	-0.05623 (29)	0.04680 (51)	0.15951 (23)
C <sub>2</sub>	-0.12996 (36)	0.09041 (33)	0.20889 (19)
C <sub>3</sub>	-0.26068 (38)	0.09719 (35)	0.19631 (22)
C <sub>4</sub>	-0.31767 (29)	0.06035 (52)	0.13434 (25)
C <sub>5</sub>	-0.24395 (38)	0.01674 (35)	0.08495 (20)
C <sub>6</sub>	-0.11323 (41)	0.00996 (35)	0.09753 (21)
Ph <sub>2</sub>			
C <sub>1</sub>	0.26843 (74)	0.38405 (36)	0.10186 (24)
C <sub>2</sub>	0.28655 (70)	0.36259 (33)	0.02864 (28)
C <sub>3</sub>	0.24052 (53)	0.41413 (36)	-0.20771 (20)
C <sub>4</sub>	0.17637 (80)	0.48713 (40)	-0.01083 (27)
C <sub>5</sub>	0.15825 (72)	0.50858 (33)	0.06239 (32)
C <sub>6</sub>	0.20428 (46)	0.45704 (30)	0.11873 (22)
PhN			
C <sub>1</sub>	-0.00313 (35)	0.23210 (46)	0.05890 (20)
C <sub>2</sub>	-0.12574 (37)	0.24896 (24)	0.08149 (16)
C <sub>3</sub>	-0.22200 (30)	0.26580 (41)	0.02940 (22)
C <sub>4</sub>	-0.19563 (37)	0.26579 (47)	-0.04528 (20)
C <sub>5</sub>	-0.07302 (40)	0.24893 (27)	-0.06787 (16)
C <sub>6</sub>	0.02323 (31)	0.23209 (42)	-0.01578 (22)

In the structure of *p*-nitroaniline,<sup>19</sup> where the mesomeric effects of the two substituents are cooperative, the C<sub>2</sub>-C<sub>3</sub> and C<sub>5</sub>-C<sub>6</sub> bonds were found to have a mean length of 1.375 (5) Å and the mean length of the C<sub>1</sub>-C<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub>, C<sub>4</sub>-C<sub>3</sub>, and C<sub>4</sub>-C<sub>5</sub> bonds was found to be 1.402 (3) Å. Thus the distortion results in deviations of the order of 0.02 Å from the distance of 1.392 Å in unsubstituted benzene. It is unlikely that we would have detected significant distortions of the order of 0.02 Å even if the positions of the individual ring atoms had

(19) K. N. Trueblood, E. Goldish, and J. Donohue, *ibid.*, **14**, 1009 (1961).

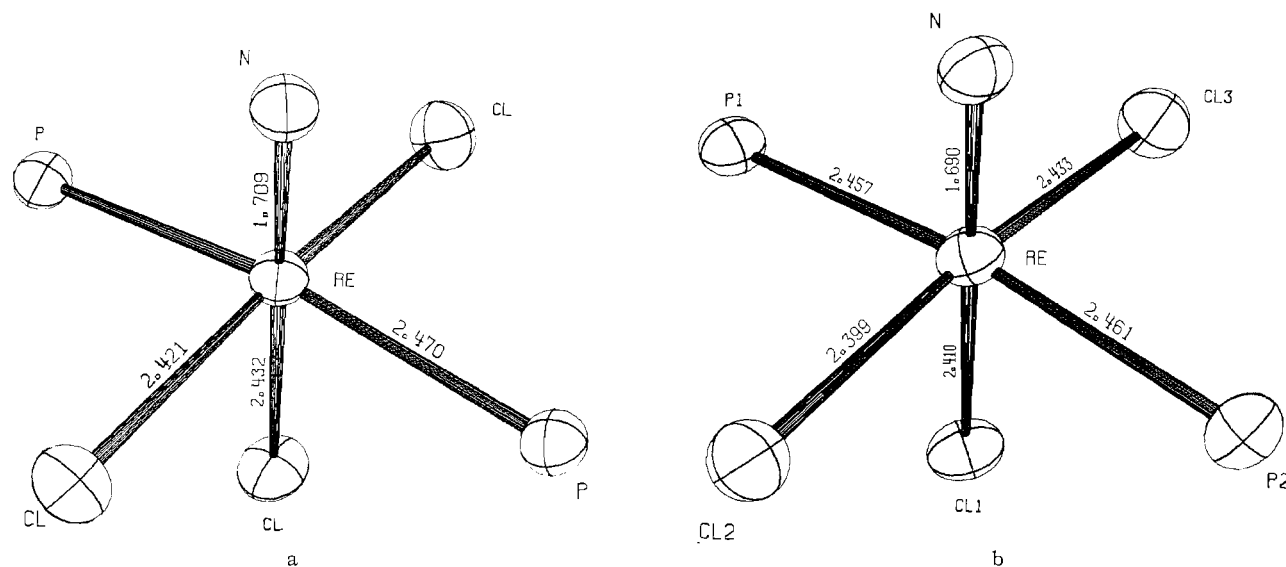


Figure 2.—Perspective drawings of the inner coordination sphere of (a)  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$  and (b)  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$ .

TABLE VIa  
CALCULATED HYDROGEN POSITIONAL PARAMETERS FOR  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$

Atom or group of attachment	x	y	z	Atom or group of attachment	x	y	z
$\text{Et}_1\text{C}_1$	-0.228	-0.151	0.132	Ph	-0.308	0.160	-0.023
	-0.248	-0.089	0.189		-0.400	0.292	-0.031
$\text{Et}_1\text{C}_2$	-0.394	-0.104	-0.006		-0.421	0.320	0.090
	-0.403	-0.159	0.062		-0.350	0.215	0.218
	-0.412	-0.054	0.059		-0.257	0.083	0.226
$\text{Et}_2\text{C}_1$	-0.298	-0.008	-0.053	PhN	0.128	0.249	0.238
	-0.192	-0.030	-0.018		0.138	0.412	0.238
$\text{Et}_2\text{C}_2$	-0.198	-0.114	-0.075		-0.100	0.432	0.264
	-0.243	-0.157	-0.028		-0.111	0.269	0.264
	-0.129	-0.128	0.031				
Me	-0.005	0.591	0.328				
	-0.014	0.660	0.259				
	-0.096	0.586	0.224				

TABLE VIb  
CALCULATED HYDROGEN POSITIONAL PARAMETERS FOR  $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$

Atom or group of attachment	x	y	z	Atom or group of attachment	x	y	z
$\text{Et}_1\text{C}_1$	0.215	-0.004	0.283	AcMe	-0.462	0.340	-0.122
	0.090	0.030	0.301		-0.465	0.282	-0.060
$\text{Et}_1\text{C}_2$	0.120	-0.127	0.244		-0.407	0.364	-0.050
	0.089	-0.113	0.321	Ph <sub>1</sub>	-0.094	0.114	0.249
	-0.005	-0.094	0.262		-0.309	0.125	0.229
$\text{Et}_2\text{C}_1$	0.122	-0.081	0.116		-0.403	0.064	0.127
	0.164	-0.014	0.067		-0.066	-0.018	0.066
$\text{Et}_2\text{C}_2$	0.321	-0.084	0.172		-0.282	-0.007	0.045
	0.335	-0.098	0.093	Ph <sub>2</sub>	0.327	0.315	0.017
	0.362	-0.016	0.125		0.252	0.400	-0.075
$\text{Et}_3\text{C}_1$	0.535	0.275	0.191		0.147	0.521	-0.048
	0.505	0.278	0.112		0.117	0.556	0.073
$\text{Et}_3\text{C}_2$	0.563	0.417	0.193		0.193	0.471	0.166
	0.649	0.382	0.139	PhN	-0.144	0.249	0.130
	0.530	0.422	0.114		-0.302	0.276	0.044
$\text{Et}_4\text{C}_1$	0.352	0.425	0.251		-0.055	0.249	-0.116
	0.235	0.380	0.269		0.103	0.222	-0.030
$\text{Et}_4\text{C}_2$	0.473	0.324	0.315				
	0.384	0.361	0.366				
	0.356	0.280	0.333				

TABLE VIIa

SELECTED INTERATOMIC DISTANCES FOR  
ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (Å)

Re-N	1.709 (4)	P-P'	4.912 (3)
Re-Cl <sub>1</sub>	2.432 (2)	P-N	3.150 (3)
Re-Cl <sub>2</sub>	2.421 (1)	P-Et <sub>1</sub> C <sub>1</sub>	1.819 (5)
Re-P	2.470 (1)	P-Et <sub>2</sub> C <sub>1</sub>	1.832 (5)
Cl <sub>1</sub> -N	4.141 (5)	P-PhC <sub>1</sub>	1.828 (6) <sup>a</sup>
Cl <sub>1</sub> -Cl <sub>2</sub>	3.336 (2)	Et <sub>1</sub> C <sub>1</sub> -Et <sub>1</sub> C <sub>2</sub>	1.522 (8)
Cl <sub>1</sub> -P	3.277 (2)	Et <sub>2</sub> C <sub>1</sub> -Et <sub>2</sub> C <sub>2</sub>	1.526 (7)
Cl <sub>2</sub> -P	3.478 (2)	Me-O	1.420 (14)
Cl <sub>2</sub> -P' <sup>b</sup>	3.419 (2)	PhNC <sub>4</sub> -O	1.334 (13) <sup>a</sup>
Cl <sub>2</sub> -Cl <sub>2</sub> '	4.835 (3)	N-PhNC <sub>1</sub>	1.373 (11) <sup>a</sup>
Cl <sub>2</sub> -N	3.040 (3)		

<sup>a</sup> These standard deviations were not calculated from the elements of the variance-covariance matrix but were estimated using the formulas of D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953). <sup>b</sup> The primed atom is related to the original atom by the twofold axis at 0, y, 1/4.

TABLE VIIb

SELECTED INTERATOMIC DISTANCES FOR  
ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (Å)

Re-N	1.690 (5)	P <sub>1</sub> -N <sub>1</sub>	3.015 (7)
Re-Cl <sub>1</sub>	2.410 (3)	P <sub>1</sub> -P <sub>2</sub>	4.905 (7)
Re-Cl <sub>2</sub>	2.399 (3)	P <sub>2</sub> -N	3.150 (6)
Re-Cl <sub>3</sub>	2.433 (3)	P <sub>1</sub> -Et <sub>1</sub> C <sub>1</sub>	1.811 (7)
Re-P <sub>1</sub>	2.457 (4)	P <sub>1</sub> -Et <sub>2</sub> C <sub>1</sub>	1.806 (7)
Re-P <sub>2</sub>	2.461 (4)	P <sub>1</sub> -Ph <sub>1</sub> C <sub>1</sub>	1.824 (10) <sup>a</sup>
Cl <sub>1</sub> -N	4.097 (7)	P <sub>2</sub> -Et <sub>3</sub> C <sub>1</sub>	1.810 (8)
Cl <sub>1</sub> -Cl <sub>2</sub>	3.295 (5)	P <sub>2</sub> -Et <sub>4</sub> C <sub>1</sub>	1.818 (8)
Cl <sub>1</sub> -Cl <sub>3</sub>	3.279 (6)	P <sub>2</sub> -Ph <sub>2</sub> C <sub>1</sub>	1.815 (9) <sup>a</sup>
Cl <sub>1</sub> -P <sub>1</sub>	3.315 (5)	Et <sub>1</sub> C <sub>1</sub> -Et <sub>3</sub> C <sub>2</sub>	1.529 (11)
Cl <sub>1</sub> -P <sub>2</sub>	3.322 (5)	Et <sub>2</sub> C <sub>1</sub> -Et <sub>2</sub> C <sub>2</sub>	1.521 (11)
Cl <sub>2</sub> -N	3.110 (7)	Et <sub>3</sub> C <sub>1</sub> -Et <sub>3</sub> C <sub>2</sub>	1.512 (11)
Cl <sub>2</sub> -Cl <sub>3</sub>	4.819 (6)	Et <sub>4</sub> C <sub>1</sub> -Et <sub>4</sub> C <sub>2</sub>	1.515 (10)
Cl <sub>2</sub> -P <sub>1</sub>	3.362 (5)	AcC-AcO	1.215 (9)
Cl <sub>2</sub> -P <sub>2</sub>	3.421 (4)	AcC-AcMe	1.447 (10)
Cl <sub>3</sub> -N	2.982 (7)	AcC-PhNC <sub>4</sub>	1.494 (12) <sup>a</sup>
Cl <sub>3</sub> -P <sub>1</sub>	3.556 (4)	N-PhNC <sub>1</sub>	1.379 (10) <sup>a</sup>
Cl <sub>3</sub> -P <sub>2</sub>	3.414 (5)		

<sup>a</sup> See footnote a of Table VIIa.

TABLE VIIIa

SELECTED INTERATOMIC ANGLES FOR  
ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (DEG)

N-Re-P	96.11 (2)	Re-P-Et <sub>1</sub> C <sub>1</sub>	113.9 (2)
N-Re-Cl <sub>2</sub>	93.16 (2)	Re-P-Et <sub>2</sub> C <sub>1</sub>	116.1 (2)
N-Re-Cl <sub>1</sub>	180	Re-P-PhC <sub>1</sub>	112.0 (3) <sup>a</sup>
P-Re-Cl <sub>1</sub>	83.89 (2)	P-Et <sub>1</sub> C <sub>1</sub> -Et <sub>1</sub> C <sub>2</sub>	115.0 (4)
Cl <sub>2</sub> -Re-Cl <sub>1</sub>	86.84 (2)	P-Et <sub>2</sub> C <sub>1</sub> -Et <sub>2</sub> C <sub>2</sub>	113.6 (3)
P-Re-Cl <sub>2</sub>	90.65 (5)	Et <sub>1</sub> C <sub>1</sub> -P-Et <sub>2</sub> C <sub>1</sub>	105.0 (2)
P'-Re-Cl <sub>2</sub>	88.68 (5)	Et <sub>1</sub> C <sub>1</sub> -P-PhC <sub>1</sub>	103.4 (3) <sup>a</sup>
P-Re-P'	167.77 (5)	Et <sub>2</sub> C <sub>1</sub> -P-PhC <sub>1</sub>	105.2 (2) <sup>a</sup>
Cl <sub>2</sub> -Re-Cl <sub>2</sub> '	173.67 (6)	N-O-Me	121.9 (6)
Re-N-O	174.65 (9)	PhNC <sub>4</sub> -O-Me	118.1 (7) <sup>a</sup>
Re-N-PHNC <sub>1</sub>	175.81 (8) <sup>a</sup>		

<sup>a</sup> See footnote a of Table VIIa.

been refined. Finally, careful inspection of difference Fourier maps gave no indication that the distortion was significant.

The Re-P distances are similar in both compounds (methoxy, 2.47 Å; acetyl, 2.46 Å), and these compare favorably with the values 2.45 and 2.48 Å found in ReOCl<sub>3</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>,<sup>17</sup> 2.45 Å in ReNCl<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>,<sup>3</sup> and 2.44, 2.45, and 2.49 Å in ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>,<sup>2</sup> although, as previously mentioned, all of

TABLE VIIIb

SELECTED INTERATOMIC ANGLES FOR  
ReCl<sub>3</sub>(NC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub>)(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (DEG)

Cl <sub>1</sub> -Re-N	175.02 (17)	Re-P <sub>1</sub> -Et <sub>1</sub> C <sub>1</sub>	114.2 (2)
Cl <sub>2</sub> -Re-Cl <sub>2</sub>	86.50 (12)	Re-P <sub>1</sub> -Et <sub>2</sub> C <sub>1</sub>	115.9 (3)
Cl <sub>1</sub> -Re-Cl <sub>3</sub>	85.23 (13)	Re-P <sub>1</sub> -Ph <sub>1</sub> C <sub>1</sub>	111.2 (4) <sup>a</sup>
Cl <sub>1</sub> -Re-P <sub>1</sub>	85.83 (10)	Re-P <sub>2</sub> -Et <sub>3</sub> C <sub>1</sub>	115.0 (2)
Cl <sub>1</sub> -Re-P <sub>2</sub>	85.98 (11)	Re-P <sub>2</sub> -Et <sub>4</sub> C <sub>1</sub>	116.6 (3)
N-Re-Cl <sub>2</sub>	97.50 (21)	Re-P <sub>2</sub> -Ph <sub>2</sub> C <sub>1</sub>	110.0 (4) <sup>a</sup>
N-Re-Cl <sub>3</sub>	90.84 (21)	P <sub>1</sub> -Et <sub>1</sub> C <sub>1</sub> -Et <sub>1</sub> C <sub>2</sub>	114.8 (5)
N-Re-P <sub>1</sub>	91.36 (19)	P <sub>1</sub> -Et <sub>2</sub> C <sub>1</sub> -Et <sub>2</sub> C <sub>2</sub>	114.3 (5)
N-Re-P <sub>2</sub>	96.99 (19)	P <sub>2</sub> -Et <sub>3</sub> C <sub>1</sub> -Et <sub>3</sub> C <sub>2</sub>	115.0 (5)
Cl <sub>2</sub> -Re-Cl <sub>3</sub>	171.59 (6)	P <sub>2</sub> -Et <sub>4</sub> C <sub>1</sub> -Et <sub>4</sub> C <sub>2</sub>	113.8 (5)
Cl <sub>2</sub> -Re-P <sub>1</sub>	87.60 (8)	Et <sub>1</sub> C <sub>1</sub> -P <sub>1</sub> -Et <sub>2</sub> C <sub>1</sub>	105.8 (3)
Cl <sub>2</sub> -Re-P <sub>2</sub>	89.46 (8)	Et <sub>1</sub> C <sub>1</sub> -P <sub>1</sub> -Ph <sub>1</sub> C <sub>1</sub>	103.9 (4) <sup>a</sup>
Cl <sub>3</sub> -Re-P <sub>1</sub>	93.30 (9)	Et <sub>2</sub> C <sub>1</sub> -P <sub>1</sub> -Ph <sub>1</sub> C <sub>1</sub>	104.8 (5) <sup>a</sup>
Cl <sub>3</sub> -Re-P <sub>2</sub>	88.45 (9)	Et <sub>3</sub> C <sub>1</sub> -P <sub>2</sub> -Et <sub>4</sub> C <sub>1</sub>	104.8 (3)
P <sub>1</sub> -Re-P <sub>2</sub>	171.45 (6)	Et <sub>3</sub> C <sub>1</sub> -P <sub>2</sub> -Ph <sub>2</sub> C <sub>1</sub>	103.9 (5) <sup>a</sup>
Re-N-AcC	171.88 (23)	Et <sub>4</sub> C <sub>1</sub> -P <sub>2</sub> -Ph <sub>2</sub> C <sub>1</sub>	105.5 (5) <sup>a</sup>
Re-N-PhNC <sub>1</sub>	171.77 (37) <sup>a</sup>	PhNC <sub>4</sub> -AcC-AcMe	119.8 (8) <sup>a</sup>
AcMe-AcC-AcO	121.51 (81)	PhNC <sub>3</sub> -AcC-AcO	118.5 (8) <sup>a</sup>

<sup>a</sup> See footnote a of Table VIIa.

these distances are long when compared with the values found in many other third-row transition metal-phosphine compounds.

The Re-Cl distances in the arylimino complexes are in agreement with the distances of 2.41–2.47 Å found in ReOCl<sub>3</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>.<sup>17</sup> However, in the arylimino compounds the Re-Cl distances *trans* to N (2.43 Å in the methoxy compound and 2.41 Å in the acetyl compound) are similar to the distances *cis* to N (2.43 Å in the methoxy compound and 2.40 and 2.43 Å in the acetyl compound). In ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub><sup>2</sup> the *cis* Re-Cl distance, 2.45 Å, is comparable with the above distances, but the distance *trans* to N is much longer at 2.56 Å.

The N-PhNC<sub>1</sub> distances, 1.38 Å in the acetyl compound and 1.37 Å in the methoxy compound, are in reasonable agreement with the distances 1.40 Å in *p*-chloroaniline,<sup>20</sup> 1.38 Å in *p*-aminobenzoic acid,<sup>21</sup> and 1.37 Å in *p*-nitroaniline.<sup>19</sup>

The geometry of the acetyl group in the acetyl compound is in agreement with the distances and angles found for the acetyl groups in 2-acetylpyridine<sup>22</sup> and N-acetylglycine.<sup>23</sup> Similarly the geometry of the methoxy group in the methoxy compound is essentially the same as the groups in deoxyanisoin,<sup>24</sup> *p,p'*-dimethoxybenzophenone,<sup>24</sup> and *p*-methoxyindophenol N-oxide.<sup>25</sup>

The P-C<sub>6</sub>H<sub>5</sub> distances in the arylimino complexes are in reasonable agreement with the corresponding distances in ReNCl<sub>2</sub>(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub><sup>2</sup> but the P-C<sub>2</sub>H<sub>5</sub> distances in the latter compound are considerably longer than those in the arylimino compounds. The P-C<sub>2</sub>H<sub>5</sub> distances in the methoxy compound are 1.82 and 1.83 Å, and those in the acetyl compound are 1.81, 1.81, 1.81, and 1.82 Å, but the distances in the nitrido

(20) J. H. Palm, *Acta Cryst.*, **21**, 473 (1966).

(21) T. F. Lai and R. E. Marsh, *ibid.*, **22**, 885 (1967).

(22) A. Laurent, *ibid.*, **21**, 710 (1966).

(23) J. Donohue and R. E. Marsh, *ibid.*, **15**, 941 (1962).

(24) H. G. Normant and I. L. Karle, *ibid.*, **15**, 873 (1962).

(25) C. Romer and B. Hesper, *ibid.*, **20**, 162 (1966).

complex range from 1.85 to 1.90 Å with a mean value of 1.87 Å.

The Re–N distances and Re–N–C angles are 1.71 Å and 175.8° in the methoxy compound and 1.69 Å and 171.9° in the acetyl compound. These distances are of the order one would expect for a Re–N double bond from the distance 1.60 Å observed for an Re–N formal triple bond in the five-coordinate complex  $\text{ReNCl}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$  but are surprisingly very much shorter than the formal triple-bond distance of 1.79 Å observed in  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ .<sup>3</sup>

### Discussion

Chatt, *et al.*,<sup>1</sup> have suggested that the systematic variation of the dipole moments of the arylimino compounds with the mesomeric properties of the group *para* to the nitrogen atom results from a drift of the nitrogen lone-pair electrons into a vacant d orbital on the rhenium atom and a compensating drift of electrons from the aromatic system to the nitrogen atom. This hypothesis suggests that the rhenium–nitrogen bond can be represented as  $\text{Re}\equiv\text{N}$  and that the order of the bond should increase as the electron-releasing power of the *para* substituent increases.

In agreement with this, the Re–N–C angle is close to 180° in both arylimino compounds studied and the deviation from linearity is greater in the acetyl compound (8.1°) than in the methoxy compound (4.2°). The Re–N distances are not in agreement. The distance in the acetyl compound, 1.690 (5) Å, is possibly significantly shorter than the distance in the methoxy compound, 1.709 (4) Å.

The compound which would be expected to bear the strongest resemblance to the arylimino compounds is  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ . However, the Re–N distance, 1.788 (11) Å, and the *trans* Re–Cl distance, 2.563(4) Å,<sup>2</sup> in this compound are very long when compared with the corresponding distances in the arylimino complexes. This extension of a pair of bonds along one axis of the octahedron suggests antibonding effects.

In spite of the fact that Re(V) is a  $d^2$  system, both the arylimino and the nitrido compounds are diamagnetic at room temperature. This suggests that there is a 5d orbital which lies considerably lower in energy than the other four. Kirkham, *et al.*,<sup>26</sup> have considered the problem of  $\text{ReOCl}_3[o\text{-C}_6\text{H}_4((\text{CH}_3)_2\text{As})_2]$ , and on the assumption that the contribution to the ligand field is the same for both arsenic and chlorine and hence the field is tetragonal, they conclude that the  $d_{xy}$  orbital would have the lowest energy ( $z$  is the Cl–Re–O axis). One might expect P to be equivalent to Cl and hence predict occupation of the  $d_{xy}$  level in  $\text{ReNCl}_2(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ . This model, however, predicts shorter bonds along the  $z$  axis, contrary to the experimental observations.

Let us suppose that it is the  $d_{zz}$  orbital which lies lowest in energy and is occupied by the rhenium electrons. A nitrogen atom on the  $z$  axis can be bonded to

TABLE IX  
PRINCIPAL ROOT-MEAN-SQUARE AMPLITUDES  
OF THERMAL VIBRATION (Å)

Atom	Minimum	Intermediate	Maximum
(a) $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{OCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$			
Re	0.1497 (4)	0.1779 (3)	0.1949 (3)
Cl <sub>1</sub>	0.154 (2)	0.231 (2)	0.275 (2)
Cl <sub>2</sub>	0.191 (1)	0.229 (1)	0.240 (1)
P	0.172 (1)	0.187 (1)	0.209 (1)
N	0.167 (6)	0.185 (6)	0.210 (6)
O	0.160 (10)	0.312 (13)	0.319 (12)
Me	0.175 (14)	0.253 (14)	0.383 (17)
Et <sub>1</sub> C <sub>1</sub>	0.180 (6)	0.252 (6)	0.266 (6)
Et <sub>1</sub> C <sub>2</sub>	0.200 (7)	0.297 (7)	0.330 (8)
Et <sub>2</sub> C <sub>1</sub>	0.192 (6)	0.214 (6)	0.244 (6)
Et <sub>2</sub> C <sub>2</sub>	0.194 (6)	0.258 (7)	0.295 (7)
(b) $\text{ReCl}_3(\text{NC}_6\text{H}_4\text{COCH}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_2$			
Re	0.1700 (6)	0.1891 (5)	0.2053 (5)
Cl <sub>1</sub>	0.175 (3)	0.232 (2)	0.262 (2)
Cl <sub>2</sub>	0.193 (3)	0.219 (3)	0.263 (2)
Cl <sub>3</sub>	0.195 (3)	0.234 (3)	0.258 (3)
P <sub>1</sub>	0.183 (3)	0.196 (3)	0.215 (3)
P <sub>2</sub>	0.185 (3)	0.202 (3)	0.229 (3)
N	0.169 (9)	0.204 (8)	0.211 (8)

the rhenium atom as follows. One pair of electrons is donated into an octahedral  $d^2sp^3$  hybrid orbital, formed from the rhenium  $5d_{z^2}$ ,  $5d_{x^2-y^2}$ ,  $6s$ ,  $6p_x$ ,  $6p_y$ , and  $6p_z$  orbitals, to give a  $\sigma$  bond. A second pair of electrons can be taken from the nitrogen into the vacant  $d_{yz}$  orbital to form a  $\pi$  bond. A third pair of nitrogen electrons will interact with the filled  $d_{zz}$  orbital resulting in antibonding repulsion and a lengthening of the bond. A similar argument can be applied to the *trans* Cl atom and again lengthening of the bond is expected. An extension of the bonds along the  $x$  axis would also be expected from this model, since the same conditions apply here as along the  $z$  axis. This has not been observed. However, it is possible that  $\pi$  bonding is much less important for these ligands than it is for nitrogen.

If we assume the  $d_{zz}$  orbital to be lowest also in the arylimino compounds then we can rationalize the observation that the Re–N distance is shorter in the acetyl compound. In the arylimino compounds the antibonding pair of electrons can escape into the aromatic system, particularly if there is an electron-withdrawing substituent in the *para* position. We thus expect a stronger bond in the acetyl complex. Although the *trans* Cl atoms in the arylimino and nitrido complexes bond similarly, in the arylimino complex, the electron "pressure" from the nitrogen atom has been reduced and since, as we have assumed,  $\pi$  bonding is of lesser importance in determining bond length, a normal Re–Cl distance is observed.

The above rationalization contains some unsatisfactory points. We are currently investigating the  $\text{OsNCl}_5^{2-}$  ion, in which the assumption of a tetragonal ligand field is valid and the  $d_{xy}$  orbital should be occupied. Boron trihalide adducts of the nitrido complex,  $\text{ReCl}_2(\text{NBX}_3)(\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5)_3$ , have also been prepared,<sup>27</sup> and these are under study. We hope that

(26) W. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 550 (1965).

(27) J. Chatt and B. Heaton, *Chem. Commun.*, 274 (1968).

such studies will provide further useful data on metal-nitrogen multiple bonds.

### Thermal Motions of the Atoms

The principal root-mean-square amplitudes of vibration for the atoms that were refined anisotropically are listed in Table IX. The directions of vibration can be seen in Figure 1. With the possible exception of the O atom and CH<sub>3</sub> group of the methoxy structure the values appear to be physically reasonable. (The O atom and CH<sub>3</sub> group are suspect because they lie very close to the C<sub>2</sub> axis in the disordered model.)

It is possible to apply "corrections" to the bond lengths assuming various vibration models.<sup>28</sup> The most reasonable model in this case would be one in which the atoms bonded to the Re atom ride on the Re atom. An alternative model allows the atoms to vibrate independently. The bond lengths after correction with these two models are shown in Table X.

It is important to keep in mind that generally the errors of assumption in the thermal model exceed the precision with which the bond lengths have been determined. The point we wish to make here is that the

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

TABLE X  
BOND LENGTHS (Å) AFTER CORRECTION FOR THERMAL VIBRATION (a) ASSUMING RIDING MODEL AND (b) ASSUMING INDEPENDENT MOTION

Bond	Methoxy			Acetyl		
	Uncor	a	b	Uncor	a	b
Re-N	1.709	1.711	1.752	1.690	1.690	1.735
Re-Cl <sub>1</sub>	2.432	2.444	2.473	2.410	2.420	2.451
Re-Cl <sub>2</sub>	2.421	2.432	2.455	2.399	2.409	2.438
Re-Cl <sub>3</sub>				2.433	2.443	2.472
Re-P <sub>1</sub>	2.470	2.473	2.497	2.457	2.459	2.487
Re-P <sub>2</sub>				2.461	2.466	2.494

difference between the Re-N distances in the methoxy and acetyl compounds is not substantially affected by choice of thermal model.

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## The Structure of Hexaamminechromium(III) Pentachlorocuprate(II), [Cr(NH<sub>3</sub>)<sub>6</sub>][CuCl<sub>5</sub>]

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The crystal structure of hexaamminechromium(III) pentachlorocuprate(II), [Cr(NH<sub>3</sub>)<sub>6</sub>][CuCl<sub>5</sub>], has been redetermined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group Fd3c of the cubic system with 32 formula units in a cell 22.240 (7) Å on an edge. The calculated density of 1.908 g/cm<sup>3</sup> agrees well with that of 1.892 g/cm<sup>3</sup> measured previously. The structure has been refined by least-squares methods to a final *R* factor on *F* of 3.7% for the 633 reflections above background. The positions of the hydrogen atoms of the ammine groups were included in this refinement. In addition, the charges on the atoms were determined. The Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ion is required crystallographically to have  $\bar{3}$  site symmetry. The coordination geometry is octahedral. The N-Cr-N angle is 89.65 (12)° and the Cr-N bond length is 2.0644 (25) Å. The [CuCl<sub>5</sub>]<sup>2-</sup> ion is required crystallographically to have 32 site symmetry and is therefore a regular trigonal bipyramid. There are two independent Cu-Cl distances, one along the threefold axis and one in the equatorial plane. The Cu-Cl bond lengths, uncorrected for the effects of thermal motion, are Cu-Cl<sub>ax</sub> = 2.2964 (12), Cu-Cl<sub>eq</sub> = 2.3912 (13) Å. This significant shortening of the axial bond lengths in a trigonal-bipyramidal MX<sub>5</sub> complex is compared with results available for other MX<sub>5</sub> complexes. This shortening may be explained by the stereochemical activity of the 3d electrons.

### Introduction

The number of authentic five-coordinate transition metal complexes has increased dramatically during the past 4 years.<sup>1</sup> In trying to formulate a systematic basis for those factors which favor a given five-coordinate structure, one discovers that most examples are complicated by the utilization of polydentate ligands,<sup>2</sup>

some of which impose their own stereochemistry on the resulting complexes.<sup>2c,3</sup> That electronic and  $\pi$ -bonding considerations may be important factors in stabilizing five-coordination has become apparent recently from

(1) For example, see the relatively recent reviews: (a) J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 380 (1965); (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966).

(2) Representative polydentate ligands are illustrated in the recent papers: (a) G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967); (b) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967); (c) Z. Dori and H. B. Gray, *ibid.*, **88**, 1394 (1966); (d) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (e) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(3) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).