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**Coordination of the Aryldiazo Ligand to Transition Metals. Structure of Chloro(bis(3-diphenylphosphinopropyl)phenylphosphine)phenyldiazorhodium Hexafluorophosphate Methylene Chloride Solvate,  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)] [\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$**

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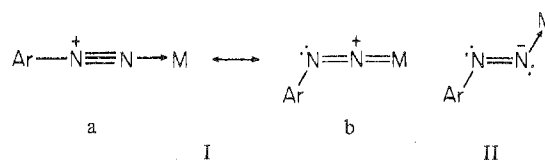
The structure of  $[\text{RhLCl}(\text{N}_2\text{C}_6\text{H}_5)] [\text{PF}_6]$  where L = the tridentate phosphine ligand  $\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2$  has been determined from three-dimensional X-ray counter data collected on a single crystal of the  $\text{CH}_2\text{Cl}_2$  solvate. The material crystallizes in space group  $C_1^1-P1$  of the triclinic system with two formula units of the complex and two solvent molecules in a cell of dimensions  $a = 12.675$  (7) Å,  $b = 13.254$  (7) Å,  $c = 15.092$  (10) Å,  $\alpha = 94.78$  (5)°,  $\beta = 99.47$  (5)°,  $\gamma = 112.40$  (8)°, and  $V = 2282.3$  Å<sup>3</sup>. The observed and calculated ( $Z = 2$ ) densities are 1.50 (1) and 1.507 g/cm<sup>3</sup>, respectively. The structure has been refined (on  $F$ ) by a full-matrix least-squares procedure to a conventional agreement index of 0.057 for 4031 observations having  $F_o^2 > 3\sigma(F_o^2)$ . The structural results reveal an ionic complex consisting of  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  cations (Ph = C<sub>6</sub>H<sub>5</sub>) and  $\text{PF}_6^-$  anions. The geometry of the cation is distorted tetragonal pyramidal with a basal plane consisting of the chloro ligand and the three P atoms of the tridentate phosphine. The apical coordination site is occupied by a doubly bent aryldiazo ligand and thus affords the first structural example of the aryldiazo analog of  $\text{NO}^-$ ,  $\text{N}_2\text{Ph}^-$ . The doubly bent geometry suggests formulation of the complex as the oxidative adduct of  $\text{N}_2\text{Ph}^+$  to  $\text{Rh}^{\text{I}}\text{LCl}$  yielding  $[\text{Rh}^{\text{III}}\text{LCl}(\text{N}_2\text{Ph})]^+$ . Distances and angles of interest within the cation are as follows: Rh-P, 2.368 (3), 2.274 (3), 2.352 (3) Å; Rh-Cl, 2.403 (2) Å; Rh-N(1) ( $\alpha$  to Rh), 1.961 (7) Å; N(1)-N(2), 1.172 (9) Å; N(2)-C(7) (Ph), 1.445 (11) Å; Rh-N(1)-N(2), 125.1 (6)°; N(1)-N(2)-C(7), 118.9 (8)°. The structural results are compared with those for the corresponding NO complex,  $[\text{RhLCl}(\text{NO})]^+$ , and with the parent complex,  $\text{RhLCl}$ . The implications of the nitrosyl-aryldiazo analogy are discussed.

**Introduction**

The coordination of aryldiazonium cations,  $\text{ArN}_2^+$ , to transition metals is a subject of current interest to inorganic chemists. The interest in these systems derives from their employment as model systems for the  $\text{N}_2$ -fixing enzyme nitrogenase<sup>1,2</sup> and because the aryldiazonium cation is formally isoelectronic with the nitrosonium cation,  $\text{NO}^+$ .

Recent structural results<sup>3</sup> have demonstrated that nitric oxide, NO, can coordinate to a transition metal in a linear fashion formally as  $\text{NO}^+$ , where it functions as a two-electron donor (Lewis base), or in a bent ( $\text{M}-\text{N}-\text{O}$  angle 120°, M = metal) arrangement formally as  $\text{NO}^-$ , where it acts as a Lewis acid, accepting an electron pair from the metal center. The last mode of nitrosyl coordination was originally suggested by Owston, *et al.*,<sup>4</sup> on the basis of an equivocal two-dimensional structure determination of nitrosylbis(dimethylthiocarbamate)cobalt. Later structural work by Hodgson, *et al.*,<sup>5</sup> firmly established the existence of the bent  $\text{M}-\text{N}-\text{O}$  linkage. A number of semiempirical interpretations of the electronic structure underlying this experimentally verified duality of nitrosyl coordination have appeared.<sup>6-8</sup> The two distinct modes of nitrosyl coordination have also led to the suggestion<sup>9,10</sup> that NO may alternately act as an electron source ( $\text{NO}^+$ ) or sink ( $\text{NO}^-$ ), a possibility which has interesting catalytic implications. Indeed, transition metal nitrosyl complexes have been found to act as catalysts for reactions as diverse as hydrogenation,<sup>9</sup> diene dimerization,<sup>11</sup> and isomerization.<sup>12</sup>

The electronic similarity between  $\text{ArN}_2^+$  and  $\text{NO}^+$  has prompted several authors to speculate that the coordinated aryldiazo group may exhibit a similar duality in bonding and function.<sup>13-15</sup> The principal canonical forms contributing to the linear ( $\text{ArN}_2^+$ ) and bent ( $\text{ArN}_2^-$ ) forms of the coordinated aryldiazo group may be formulated, by analogy with  $\text{NO}^+$  and  $\text{NO}^-$ , as I and II. Only three structural reports of coordinated



aryldiazo groups have appeared and all involve a linear  $\text{M}-\text{N}-\text{N}$  arrangement with Ib clearly predominant.<sup>13,16,17</sup> Recent work by Bowden, *et al.*,<sup>18</sup> has led these authors to suggest that in the complex  $[\text{Ru}(\text{bipy})_2(\text{N}_2\text{Ar}')\text{Cl}] [\text{PF}_6]_2$  (bipy = 2,2'-bipyridine;  $\text{Ar}' = p\text{-C}_6\text{H}_4\text{CH}_3$  or  $p\text{-C}_6\text{H}_4\text{OCH}_3$ ) the coordinated aryldiazo group may be of the Ia form. In  $\text{Ru}(\text{X})\text{Cl}_3(\text{P})_2$  (P =  $\text{PCH}_3(\text{C}_6\text{H}_5)_2$  or  $\text{P}(\text{C}_6\text{H}_5)_3$ ; X = NO or  $p\text{-N}_2\text{C}_6\text{H}_4\text{CH}_3$ ) both the nitrosyl<sup>19</sup> and aryldiazo<sup>13</sup> complexes have been characterized and, as expected, an angle of  $\sim 180^\circ$  is found at the N atom bound to the metal in both cases.

Recently the synthesis and characterization of a series of Rh(I) complexes of the tridentate chelating ligand  $\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2$ , hereafter designated L, have been reported.<sup>20</sup>

The parent complex,  $\text{RhLCl}$ , has been found to undergo facile addition reactions with a variety of Lewis acids, A (A =  $\text{H}^+$ ,  $\text{NO}^+$ ,  $\text{N}_2\text{C}_6\text{H}_5^+$ ,  $\text{CH}_3\text{CO}^+$ ), yielding the five-coordinate cationic complexes  $[\text{RhLCl}\cdot\text{A}]^+$ .<sup>20</sup> The structure determination of the nitrosyl complex  $[\text{RhLCl}(\text{NO})] [\text{PF}_6]$ <sup>20</sup> revealed a tetragonal-pyramidal cation with the nitrosyl group occupying the apical position of the coordination sphere. The  $\text{Rh}-\text{N}-\text{O}$  angle of 131° suggests that the complex may formally be viewed as one of  $\text{Rh}(\text{III})$  and  $\text{NO}^-$ . The corresponding aryldiazo complex  $[\text{RhLCl}(\text{N}_2\text{C}_6\text{H}_5)]^+$ <sup>20</sup> is thus a prime candidate for X-ray structural investigation in order to establish that  $\text{ArN}_2^+$  is capable of the same duality in bonding as is  $\text{NO}^+$ .

In order to provide verification of the aryldiazo analog of

**Table I.** Data Collection Details for [Rh(C<sub>6</sub>H<sub>5</sub>P((CH<sub>2</sub>)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>))<sub>2</sub>]Cl(N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)[PF<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>

Molecular formula	RhCl <sub>3</sub> P <sub>4</sub> F <sub>6</sub> N <sub>2</sub> C <sub>43</sub> H <sub>44</sub>
Radiation	Mo Kα, λ 0.71069 Å
Monochromator	Graphite (002)
Takeoff angle	2.0°
Scan rate	2°/min
Receiving aperture	4.5 × 4.5 mm, 31 cm from crystal
Data collection limits	3° ≤ 2θ ≤ 41.5°; ±h, ±k, -l
Scan range	-0.70° to +0.80°, 3° ≤ 2θ ≤ 20°
(relative to Kα <sub>1</sub> , Kα <sub>2</sub> )	-0.90° to +0.80°, 20° < 2θ ≤ 31°
	-1.0° to +0.80°, 31° < 2θ ≤ 40°
	-1.3° to +0.80°, 40° < 2θ ≤ 41.5°
Background times	10 sec at scan limits 3° ≤ 2θ ≤ 31°
	20 sec at scan limits 31° < 2θ ≤ 41.5°
Attenuators	Cu foil, ratio ~2.3; inserted at 7000 counts/sec
Standards	6 every 100 reflections; 3% decay
No. of Data	5195

NO<sup>-</sup> the structure determination of [Rh(C<sub>6</sub>H<sub>5</sub>P((CH<sub>2</sub>)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>))<sub>2</sub>]Cl(N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)[PF<sub>6</sub>] was undertaken. The results of this study have appeared in preliminary form<sup>21</sup> and are reported in detail here.

### Experimental Section

Orange crystals of [Rh(C<sub>6</sub>H<sub>5</sub>P((CH<sub>2</sub>)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>))<sub>2</sub>]Cl(N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)[PF<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub> were prepared as described previously.<sup>20</sup> Preliminary photographic work failed to establish the presence of any symmetry elements higher than the trivial  $\bar{1}$  and the crystals were tentatively assigned to the triclinic system. The mosaic spread of a large number (~25) of optically satisfactory crystals was examined on a diffractometer by open-counter narrow-source ω scans<sup>22</sup> of several strong reflections. The widths at half-height were extremely anisotropic, typically varying from 0.40 to 1.50°. Finally, one crystal was examined which showed half-widths of 0.10, 0.13, and 0.10° for three non-coplanar reflections and was deemed acceptable for data collection. The crystal shows the four faces belonging to the forms {100} and {010}, an {011} face, and an {01 $\bar{1}$ } face based on a convenient cell, *vide infra*, derived from the photographic work. The crystal had dimensions 0.20 × 0.14 × 0.84 mm along the principal crystallographic directions and a calculated volume of 0.0173 mm<sup>3</sup>. Accurate lattice constants at 22° for the previously adopted cell were determined from a least-squares refinement<sup>23</sup> of the setting angles of 12 reflections (26° ≤ 2θ ≤ 28°) which had been hand-centered on a Picker four-circle diffractometer using monochromatized Mo Kα<sub>1</sub> radiation (λ 0.70930 Å) at a takeoff angle of 1.5°. They are a = 12.675 (7) Å, b = 13.254 (7) Å, c = 15.092 (10) Å, α = 94.78 (5)°, β = 99.47 (5)°, γ = 112.40 (8)°, and V = 2282.3 Å<sup>3</sup>. Cell reduction<sup>24</sup> failed to detect the presence of a cell of higher symmetry. The conventional reduced form<sup>24</sup> of the cell is related to the original cell by the matrix (010/001/100). The observed density, 1.50 (1) g/cm<sup>3</sup>, measured by flotation in a CCl<sub>4</sub>-C<sub>6</sub>H<sub>14</sub> mixture agrees well with 1.507 g/cm<sup>3</sup> calculated for two formula units of the complex and two solvent molecules (CH<sub>2</sub>Cl<sub>2</sub>) in the unit cell. With Z = 2 no crystallographic symmetry is *a priori* imposed on the complex or the solvent molecule in the triclinic cell. The centrosymmetric space group C<sub>1</sub><sup>1</sup>-P $\bar{1}$  was assumed throughout the structure determination and refinement.

Intensity data were collected by the θ-2θ scan technique<sup>22</sup> on a computer-controlled Picker FACS-I automatic diffractometer with the c axis of the crystal approximately coincident with the diffractometer spindle axis. Pertinent data collection details are given in Table I. During data collection a decrease in the intensity of the standard reflections accompanied by an increase in the mosaic spread was observed. The data collection conditions were modified accordingly (Table I). Data collection was terminated at 2θ = 41.5° because beyond that point fewer than 15% of the reflections were observable.

The 5195 data were processed as previously described.<sup>23,25</sup> The value of p was 0.04. The values of I and σ(I) were corrected for Lorentz, polarization, decomposition, and absorption effects (μ = 7.39 cm<sup>-1</sup>, Mo Kα) thereby yielding 4188 reflections which were judged observed (F<sub>o</sub><sup>2</sup> > 3σ(F<sub>o</sub><sup>2</sup>)). The transmission factors varied from 0.86 to 0.93. Of the 4188 observed data 157 pairs are centrosymmetrically equivalent. The symmetry-equivalent reflections were eliminated and the remaining 4031 reflections were used as the basis for the subsequent refinement of the structure.

### Solution and Refinement of the Structure

The structure was solved by a combination of Patterson, transformation, and Fourier methods. Trial positions for the heavy atoms (Rh, P, Cl) of the cation were located from the analysis of a three-dimensional origin-removed Patterson function. Suitable positions for the C atoms of the tridentate phosphine ligand, L, were derived by a transformation technique<sup>26</sup> based on the assumption that the cationic portion of the complex is isostructural (except for one coordination site) with the corresponding nitrosyl complex, [RhClCl(NO)]<sup>+</sup>.<sup>20</sup> A difference Fourier map, based on these atomic positions, revealed the aryldiazo group at the apical coordination site of the tetragonal-pyramidal cation, the nonhydrogen atoms of the solvent of crystallization (CH<sub>2</sub>Cl<sub>2</sub>), and the atoms of the PF<sub>6</sub><sup>-</sup> anion.

The trial structure was refined (on F) by a full-matrix least-squares procedure<sup>27</sup> in space group C<sub>1</sub><sup>1</sup>-P $\bar{1}$ . The function minimized is Σw(|F<sub>o</sub> - |F<sub>c</sub>||<sup>2</sup>) where the weights, w, are taken as 4F<sub>o</sub><sup>2</sup>/σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) and |F<sub>o</sub> and |F<sub>c</sub> are the observed and calculated structure amplitudes. Two cycles of refinement of an overall scale factor, the positional parameters for the complete trial structure, and an isotropic thermal parameter for each atom resulted in convergence with R<sub>1</sub> = 0.087 and R<sub>2</sub> = 0.121. Here, the agreement indices, R<sub>1</sub> and R<sub>2</sub>, are defined as Σ||F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>| and (Σw(|F<sub>o</sub> - |F<sub>c</sub>||<sup>2</sup>)/ΣwF<sub>o</sub><sup>2</sup>)<sup>1/2</sup>, respectively. During the refinement the five phenyl rings of the tridentate phosphine ligand were treated as rigid groups possessing D<sub>6h</sub> symmetry (C-C bond length 1.392 Å). The neutral-atom scattering factors for Rh, Cl, P, F, N, and C were taken from the usual tabulation<sup>28a</sup> while for H those of Stewart, *et al.*,<sup>28b</sup> were used. The anomalous terms for Rh, Cl, and P were those of Cromer and Liberman<sup>28c</sup> and were included in F<sub>c</sub>.<sup>29</sup>

A subsequent difference map clearly revealed all of the 44 independent H atoms. In addition there were indications of disorder in the PF<sub>6</sub><sup>-</sup> anion. There were alternative positions for each of the six F atoms of the PF<sub>6</sub><sup>-</sup> ion, presumably as a result of orientational disorder. The heights of these alternative F peaks were approximately one-fourth of those located in the initial difference map. For purposes of least-squares refinement the following model for the disorder was adopted: (1) two arrays consisting of six F atoms each were treated as individual rigid groups (O<sub>h</sub> symmetry, P-F distance 1.58 Å) with the origin of each of the groups constrained to be coincident with the P atom and only the three orientational parameters<sup>30</sup> for each group allowed to refine; (2) an overall isotropic thermal parameter was assigned to all 12 F atoms and allowed to refine; (3) an occupancy factor, α, was assigned to the group representing the major contribution to the electron density and the other group was constrained to have an occupancy factor of 1 - α with α being refined.

The positions of each of the 44 H atoms were idealized<sup>31</sup> and their contributions to F<sub>c</sub> were computed. Two cycles of refinement of an anisotropic thermal model for all nongroup atoms and an isotropic thermal model for all group atoms, including the fixed H contributions to F<sub>c</sub>, converged to agreement indices, R<sub>1</sub> and R<sub>2</sub>, of 0.057 and 0.078, respectively. The occupancy factor, α, of the major component of the PF<sub>6</sub><sup>-</sup> disorder refined to a value of 0.801 (6). The standard deviation of an observation of unit weight, based on 276 variables and 4031 observations, is 2.68 e. A final difference Fourier map shows six peaks ranging from 0.8 to 1.0 e/Å<sup>3</sup> which are associated with a third component of the disordered PF<sub>6</sub><sup>-</sup> ion. The next highest residual peak is 0.7 e/Å<sup>3</sup> which may be compared to 3.0 e/Å<sup>3</sup>, the average height of a C atom in this structure. A comparison of Σw(|F<sub>o</sub> - |F<sub>c</sub>||<sup>2</sup>) for various classes of reflections based on Miller indices, |F<sub>o</sub>|, and setting angles shows no significant dependence on any of these quantities. The parameters obtained from the final cycle of refinement are given in Tables II and III along with their estimated standard deviations as obtained from the inverse matrix. The derived parameters for the rigid-group atoms are reported in Table IV. The idealized positions for the 44 H atoms will be found in Table V.<sup>32</sup> The root-mean-square amplitudes of vibration of the 23 atoms refined anisotropically are given in Table VI. A tabulation of observed and calculated structure amplitudes is available.<sup>32</sup>

### Description of the Structure

**The Crystal Structure.** The crystal structure consists of an assemblage of discrete cations, [RhClCl(N<sub>2</sub>Ph)]<sup>+</sup>, anions, [PF<sub>6</sub>]<sup>-</sup>, and solvent molecules, CH<sub>2</sub>Cl<sub>2</sub>. The crystal packing is dominated by nonbonded interactions involving the bulky cations which are situated about the lattice points (000). The

**Table II.** Positional and Thermal Parameters for the Nongroup Atoms of  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ 

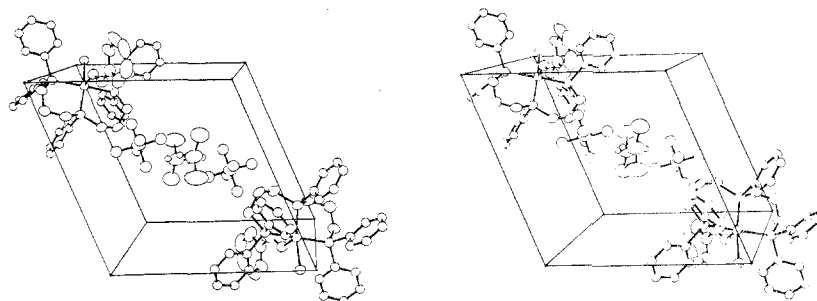
Atom	$x^a$	$y$	$z$	$\beta_{11}^b$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rh	0.05736 (5)	-0.10761 (5)	0.22635 (4)	60.7 (6)	47.6 (6)	34.1 (4)	21.9 (4)	7.9 (4)	8.3 (3)
Cl(1)	0.0980 (2)	0.0404 (2)	0.1382 (1)	77 (2)	60 (2)	49 (1)	29 (2)	19 (1)	21 (1)
Cl(2) <sup>c</sup>	0.3171 (4)	0.3250 (3)	0.2423 (3)	211 (5)	132 (4)	176 (4)	47 (4)	33 (4)	3 (3)
Cl(3) <sup>c</sup>	0.4316 (5)	0.5575 (4)	0.2412 (4)	357 (8)	154 (4)	164 (4)	83 (5)	98 (5)	71 (3)
P(1)	-0.0955 (2)	-0.0646 (2)	0.2662 (1)	65 (2)	57 (2)	35 (1)	24 (2)	11 (1)	9 (1)
P(2)	-0.0182 (2)	-0.2715 (2)	0.2775 (2)	83 (2)	56 (2)	44 (1)	27 (2)	9 (1)	14 (1)
P(3)	0.1947 (2)	-0.1573 (2)	0.1675 (2)	66 (2)	58 (2)	44 (1)	29 (2)	6 (1)	6 (1)
P(4) <sup>d</sup>	-0.2932 (2)	0.4181 (2)	0.4660 (2)	133 (3)	71 (2)	71 (2)	27 (2)	26 (2)	9 (2)
N(1)	0.1676 (6)	-0.0266 (6)	0.3409 (5)	89 (8)	74 (7)	48 (5)	35 (6)	8 (5)	13 (4)
N(2)	0.2121 (7)	-0.0657 (6)	0.3941 (5)	112 (9)	88 (7)	46 (5)	40 (7)	3 (5)	6 (5)
C(1) <sup>e</sup>	-0.1436 (8)	-0.1124 (7)	0.3693 (6)	96 (9)	67 (8)	41 (5)	22 (7)	23 (5)	12 (5)
C(2)	-0.1723 (8)	-0.2324 (8)	0.3784 (6)	106 (10)	89 (9)	49 (6)	35 (8)	30 (6)	17 (5)
C(3)	-0.0690 (8)	-0.2668 (7)	0.3832 (6)	117 (10)	62 (7)	51 (5)	30 (7)	25 (6)	25 (5)
C(4)	0.2429 (8)	-0.2506 (7)	0.2305 (6)	84 (9)	79 (8)	52 (5)	37 (7)	0 (6)	13 (5)
C(5)	0.1452 (9)	-0.3581 (7)	0.2378 (7)	113 (10)	66 (8)	79 (7)	55 (8)	13 (7)	22 (6)
C(6)	0.0757 (8)	-0.3454 (7)	0.3079 (7)	104 (10)	75 (8)	68 (6)	45 (8)	17 (7)	30 (6)
C(7)	0.3009 (8)	0.0062 (9)	0.4709 (6)	90 (10)	108 (10)	36 (5)	43 (8)	0 (6)	4 (6)
C(8)	0.3405 (11)	-0.0452 (11)	0.5352 (8)	157 (14)	170 (14)	62 (7)	102 (12)	7 (9)	21 (9)
C(9)	0.4258 (12)	0.0246 (16)	0.6130 (8)	146 (16)	256 (21)	55 (8)	123 (16)	-7 (9)	27 (11)
C(10)	0.4624 (10)	0.1379 (16)	0.6191 (10)	85 (12)	233 (21)	73 (10)	53 (14)	-9 (8)	-29 (12)
C(11)	0.4234 (11)	0.1828 (11)	0.5543 (8)	101 (12)	168 (15)	53 (7)	-13 (11)	11 (8)	-7 (9)
C(12)	0.3437 (8)	0.1209 (9)	0.4791 (6)	89 (10)	90 (10)	49 (6)	4 (8)	7 (6)	0 (6)
C(13) <sup>c</sup>	0.4090 (12)	0.4534 (10)	0.3053 (10)	214 (19)	115 (12)	117 (10)	68 (13)	40 (11)	28 (9)

<sup>a</sup> Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The quantities given in the table are the thermal coefficients  $\times 10^3$ . <sup>c</sup> These are the atoms of the methylene chloride solvate. <sup>d</sup> P(4) is the phosphorus atom of the  $\text{PF}_6^-$  anion. <sup>e</sup> C(1)–C(6) are the carbon atoms of the propyl bridges of the tridentate phosphine ligand.

**Table III.** Rigid-Group Parameters for  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ 

Group	$x_c^a$	$y_c$	$z_c$	$\delta^b$	$\epsilon$	$\eta$
P(1)R1	-0.0468 (3)	0.1886 (3)	0.3309 (3)	0.381 (3)	-2.857 (4)	-2.921 (4)
P(1)R2	-0.3184 (3)	-0.1664 (3)	0.0994 (3)	1.766 (4)	2.971 (3)	1.808 (4)
P(2)R1	-0.2426 (4)	-0.4343 (3)	0.1273 (3)	1.453 (7)	2.147 (4)	-0.830 (7)
P(3)R1	0.4443 (3)	0.0388 (3)	0.1711 (3)	-1.575 (4)	2.645 (3)	-0.616 (4)
P(3)R2	0.0921 (3)	-0.2844 (3)	-0.0384 (3)	2.948 (5)	2.364 (4)	2.293 (5)
PF6 <sup>c</sup>	-0.2932	0.4181	0.4660	-1.701 (4)	2.824 (4)	3.355 (4)
PF6' <sup>c,d</sup>	-0.2932	0.4181	0.4660	-1.39 (2)	-2.92 (2)	1.52 (2)

<sup>a</sup>  $x_c$ ,  $y_c$ , and  $z_c$  are the fractional coordinates of the rigid-group centers. <sup>b</sup> The angles  $\delta$ ,  $\epsilon$ , and  $\eta$  (radians) have been defined previously; see ref 30. <sup>c</sup> The origin of coordinates for the  $\text{PF}_6^-$  group was constrained to be coincident with P(4). <sup>d</sup> The primed  $\text{PF}_6$  group is the alternative (disordered) orientation with an occupancy factor of 0.199 (see text).



**Figure 1.** A stereoscopic view of the contents of the unit cell of  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ . The origin is at the lower left rear. The  $x$  axis is horizontal, the  $y$  axis is vertical, and the  $z$  axis points out of the plane of the paper. The shapes of the atoms in this and following drawings represent 50% probability contours of thermal motion. The H atoms of the cation have been omitted for the sake of clarity.

anions and solvent molecules occupy voids in the cation framework about the body-centered positions ( $1/2, 1/2, 1/2$ ) of the cell. The resulting arrangement is depicted in Figure 1. All intermolecular cation–cation, anion–anion, and solvent–solvent contacts are greater than the sum of the van der Waals radii for the respective atoms. There are two short anion–cation contacts, 2.38 and 2.30 Å, between F atoms of the anions and phenyldiazo H atoms of the surrounding cations. Note, however, that these H atom positions have been idealized and thus the short contacts may be in error by at least  $\pm 0.15$  Å.

**The Molecular Structure.** A stereoscopic view of the  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  cation is presented in Figure 2. A per-

spective view of the coordinatively linked phenyldiazo group together with the remainder of the inner coordination sphere about the Rh atom is shown in Figure 3. A selection of interatomic distances and angles will be found in Table VII. The details of the anion and the solvent of crystallization are of little importance in this study and will not be commented upon further other than to note that the C–Cl distances and the Cl–C–Cl angle are within the range expected for dichloromethane.<sup>33</sup> Of specific interest is the structure of the  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  cation and, in particular, the angular details of the Rh–N–N–Ph linkage.

The geometry about the Rh atom is distorted tetragonal pyramidal with the phenyldiazo function occupying the apical

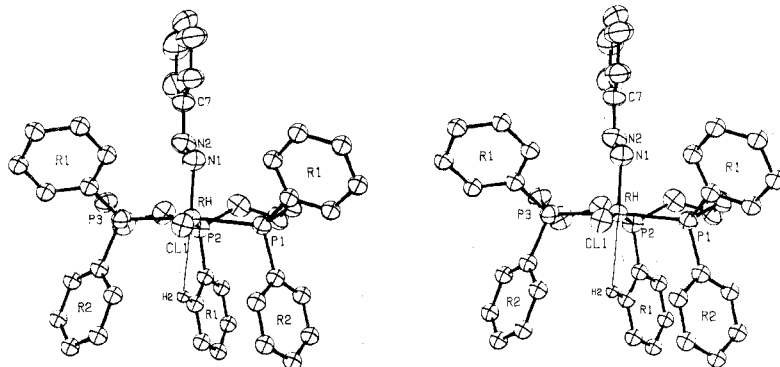


Figure 2. A stereoscopic view of an individual cation of  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ . The H atoms have been omitted for the sake of clarity except for P(2)R1H(2) which blocks the sixth coordination site of the Rh atom.

Table IV. Derived Parameters for the Rigid-Group Carbon and Fluorine Atoms of

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>
F(1) <sup>a</sup>	-0.2848 (5)	0.5358 (2)	0.4464 (4)	11.5 <sup>b</sup>
F(2)	-0.4232 (2)	0.3865 (5)	0.4773 (5)	11.5
F(3)	-0.3017 (5)	0.3003 (2)	0.4857 (4)	11.5
F(4)	-0.1633 (2)	0.4497 (5)	0.4548 (5)	11.5
F(5)	-0.2476 (6)	0.4649 (5)	0.5711 (1)	11.5
F(6)	-0.3388 (6)	0.3712 (5)	0.3609 (1)	11.5
F(1)'	-0.3214 (26)	0.4069 (24)	0.5638 (9)	11.5
F(2)'	-0.4257 (8)	0.3444 (17)	0.4213 (20)	11.5
F(3)'	-0.2650 (26)	0.4292 (24)	0.3683 (9)	11.5
F(4)'	-0.1608 (8)	0.4918 (17)	0.5108 (20)	11.5
F(5)'	-0.2668 (23)	0.3108 (13)	0.4657 (16)	11.5
F(6)'	-0.3197 (23)	0.5253 (13)	0.4664 (16)	11.5
P(1)R1C(1) <sup>c</sup>	-0.0657 (5)	0.0813 (3)	0.2955 (4)	3.3 (2)
P(1)R1C(2)	-0.1597 (4)	0.1118 (4)	0.2927 (4)	5.3 (2)
P(1)R1C(3)	-0.1408 (5)	0.2191 (5)	0.3281 (5)	6.2 (2)
P(1)R1C(4)	-0.0279 (5)	0.2959 (4)	0.3662 (4)	5.4 (2)
P(1)R1C(5)	0.0661 (4)	0.2655 (4)	0.3690 (4)	5.0 (2)
P(1)R1C(6)	0.0472 (4)	0.1582 (5)	0.3337 (4)	4.3 (2)
P(1)R2C(1)	-0.2238 (4)	-0.1213 (4)	0.1731 (3)	3.3 (2)
P(1)R2C(2)	-0.3326 (5)	-0.1910 (5)	0.1857 (3)	4.1 (2)
P(1)R2C(3)	-0.4273 (4)	-0.2360 (5)	0.1121 (4)	5.3 (2)
P(1)R2C(4)	-0.4131 (4)	-0.2114 (5)	0.0258 (3)	5.0 (2)
P(1)R2C(5)	-0.3043 (5)	-0.1418 (5)	0.0131 (3)	4.7 (2)
P(1)R2C(6)	-0.2096 (4)	-0.0967 (4)	0.0868 (4)	4.0 (2)
P(2)R1C(1)	-0.1435 (4)	-0.3664 (5)	0.1923 (3)	3.9 (2)
P(2)R1C(2)	-0.1582 (5)	-0.3430 (4)	0.1041 (4)	4.5 (2)
P(2)R1C(3)	-0.2573 (6)	-0.4108 (6)	0.0390 (3)	6.4 (2)
P(2)R1C(4)	-0.3416 (5)	-0.5022 (5)	0.0622 (4)	6.8 (3)
P(2)R1C(5)	-0.3269 (5)	-0.5256 (5)	0.1505 (5)	6.8 (3)
P(2)R1C(6)	-0.2278 (6)	-0.4578 (5)	0.2155 (3)	5.8 (2)
P(3)R1C(1)	0.3349 (4)	-0.0438 (4)	0.1676 (4)	3.6 (2)
P(3)R1C(2)	0.4104 (5)	-0.0641 (4)	0.1184 (4)	4.9 (2)
P(3)R1C(3)	0.5199 (5)	0.0186 (5)	0.1219 (4)	5.5 (2)
P(3)R1C(4)	0.5538 (4)	0.1215 (4)	0.1745 (4)	5.4 (2)
P(3)R1C(5)	0.4783 (5)	0.1418 (3)	0.2237 (4)	5.0 (2)
P(3)R1C(6)	0.3688 (4)	0.0591 (4)	0.2202 (4)	3.9 (2)
P(3)R2C(1)	0.1398 (5)	-0.2289 (4)	0.0504 (3)	3.6 (2)
P(3)R2C(2)	0.1587 (5)	-0.3220 (5)	0.0221 (4)	5.7 (2)
P(3)R2C(3)	0.1110 (6)	-0.3776 (5)	-0.0668 (4)	6.4 (2)
P(3)R2C(4)	0.0444 (6)	-0.3400 (5)	-0.1273 (3)	7.0 (3)
P(3)R2C(5)	0.0255 (5)	-0.2468 (5)	-0.0990 (4)	5.9 (2)
P(3)R2C(6)	0.0732 (5)	-0.1913 (4)	-0.0101 (4)	4.5 (2)

<sup>a</sup> F(1)–F(6) are the fluorine atoms of the PF<sub>6</sub> group with a refined occupancy factor of 0.801 (6). F(1)'–F(6)' are fluorine atoms of the PF<sub>6</sub> group with an occupancy factor of 0.199. The assumed P–F distance is 1.58 Å in both cases. <sup>b</sup> The thermal parameters for the fluorine atoms are equal to the overall (group) thermal parameter for the unprimed PF<sub>6</sub> group (see text). <sup>c</sup> C(1) is attached to P and the atoms of the ring are numbered sequentially with C(4) para to P.

coordination site and a basal plane consisting of the P atoms of the chelating triphosphine, L, and a Cl ligand. The four atoms at the base do not form a perfect plane apparently as the result of nonbonded interactions between the chloro ligand and the phenyldiazo group (*vide infra*). Nevertheless, it is

Table VI. Root-Mean-Square Amplitudes of Vibration along Principal Ellipsoid Axes (Å)

Atom	Min	Intermed	Max
Rh	0.183 (1)	0.194 (1)	0.205 (1)
Cl(1)	0.188 (3)	0.222 (3)	0.244 (3)
Cl(2)	0.309 (4)	0.393 (5)	0.449 (5)
Cl(3)	0.292 (5)	0.420 (5)	0.507 (6)
P(1)	0.195 (3)	0.207 (3)	0.209 (3)
P(2)	0.191 (3)	0.222 (3)	0.244 (3)
P(3)	0.195 (3)	0.207 (3)	0.230 (3)
P(4)	0.229 (4)	0.274 (4)	0.315 (4)
N(1)	0.21 (1)	0.24 (1)	0.25 (1)
N(2)	0.22 (1)	0.25 (1)	0.28 (1)
C(1)	0.19 (1)	0.23 (1)	0.27 (1)
C(2)	0.21 (1)	0.26 (1)	0.28 (1)
C(3)	0.18 (1)	0.25 (1)	0.29 (1)
C(4)	0.20 (1)	0.24 (1)	0.27 (1)
C(5)	0.18 (1)	0.28 (1)	0.30 (1)
C(6)	0.20 (1)	0.26 (1)	0.29 (1)
C(7)	0.19 (2)	0.25 (1)	0.29 (1)
C(8)	0.23 (2)	0.29 (1)	0.37 (2)
C(9)	0.19 (2)	0.31 (2)	0.44 (2)
C(10)	0.22 (2)	0.29 (2)	0.45 (2)
C(11)	0.22 (2)	0.26 (2)	0.43 (2)
C(12)	0.21 (1)	0.25 (1)	0.32 (1)
C(13)	0.28 (2)	0.35 (2)	0.38 (2)

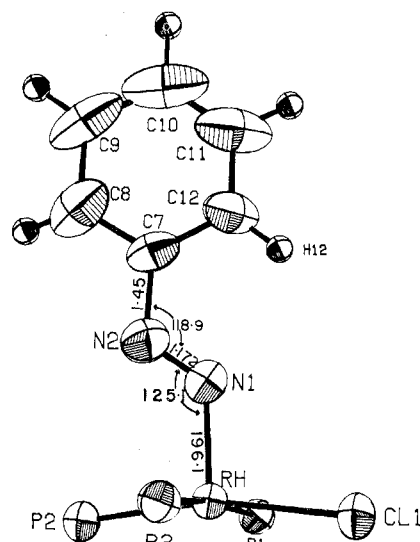


Figure 3. A perspective view of the inner coordination sphere of the  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)]^+$  cation. The methylene C atoms of the tridentate chelating ligand have been omitted for the sake of clarity.

convenient to define a mean basal plane based on these four atomic positions to aid in assessing the strength of the interaction between the Rh atom and the apical ligand. The equation of the best least-squares plane through the four basal

Table VII. Interatomic Distances (Å) and Angles (deg) in  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ 

Atoms	Distance	Atoms	Angle	Mean
Rh-Cl(1)	2.403 (2)	P(1)-Rh-P(2)	88.94 (9)	
Rh-P(1)	2.368 (3)	P(1)-Rh-P(3)	172.64 (8)	
Rh-P(2)	2.274 (3)	P(1)-Rh-Cl(1)	88.54 (8)	
Rh-P(3)	2.352 (3)	P(2)-Rh-P(3)	92.15 (9)	
Rh-N(1)	1.961 (7)	P(2)-Rh-Cl(1)	165.18 (8)	
N(1)-N(2)	1.172 (9)	P(3)-Rh-Cl(1)	88.55 (8)	
N(2)-C(7)	1.445 (11)	N(1)-Rh-P(1)	93.5 (2)	
C(7)-C(8)	1.37 (1)	N(1)-Rh-P(2)	95.8 (2)	
C(8)-C(9)	1.43 (2)	N(1)-Rh-P(3)	93.6 (2)	
C(9)-C(10)	1.38 (2)	N(1)-Rh-Cl(1)	98.9 (2)	
C(10)-C(11)	1.31 (2)	Rh-N(1)-N(2)	125.1 (6)	
C(11)-C(12)	1.35 (1)	N(1)-N(2)-C(7)	118.9 (8)	
C(12)-C(7)	1.39 (1)	N(2)-C(7)-C(8)	116.0 (10)	
P(1)-C(1)	1.837 (9)	N(2)-C(7)-C(12)	122.1 (8)	
P(1)-P(1)R1C(1)	1.823 (6)	C(7)-C(8)-C(9)	116.8 (12)	
P(1)-P(1)R2C(1)	1.827 (5)	C(8)-C(9)-C(10)	118.9 (11)	
P(2)-C(3)	1.821 (10)	C(9)-C(10)-C(11)	121.7 (13)	
P(2)-C(6)	1.836 (9)	C(10)-C(11)-C(12)	121.7 (13)	
P(2)-P(2)R1C(1)	1.815 (5)	C(11)-C(12)-C(7)	118.9 (10)	
P(3)-C(4)	1.840 (9)	C(12)-C(7)-C(8)	121.8 (9)	
P(3)-P(3)R1C(1)	1.839 (5)	Rh-P(1)-C(1)	116.4 (3)	
P(3)-P(3)R2C(1)	1.822 (6)	Rh-P(1)-P(1)R1C(1)	117.0 (2)	114.5
C(1)-C(2)	1.51 (1)	Rh-P(1)-P(1)R2C(1)	110.0 (2)	
C(2)-C(3)	1.53 (1)	C(1)-P(1)-P(1)R1C(1)	98.9 (4)	
C(4)-C(5)	1.52 (1)	C(1)-P(1)-P(1)R2C(1)	107.2 (3)	104.0
C(5)-C(6)	1.52 (1)	P(1)R1C(1)-P(1)-P(1)R2C(1)	106.0 (3)	
C(13)-Cl(2)	1.74 (1)	Rh-P(2)-C(3)	116.1 (3)	
C(13)-Cl(3)	1.71 (1)	Rh-P(2)-C(6)	119.2 (3)	114.7
Nonbonding Distances				
Rh-N(2)	2.804 (8)	Rh-P(2)-P(2)R1C(1)	108.9 (2)	
Rh-P(2)R1H(2)	2.82	C(3)-P(2)-C(6)	98.6 (4)	
N(1)-H(12)	2.45	C(3)-P(2)-P(2)R1C(1)	106.2 (3)	103.8
N(2)-H(12)	2.61	C(6)-P(2)-P(2)R1C(1)	106.7 (3)	
N(2)-H(8)	2.60	Rh-P(3)-C(4)	114.4 (3)	
P(1)-P(2)	3.253 (3)	Rh-P(3)-P(3)R1C(1)	116.4 (2)	114.6
P(1)-Cl(1)	3.331 (3)	Rh-P(3)-P(3)R2C(1)	113.0 (3)	
P(3)-P(2)	3.333 (4)	C(4)-P(3)-P(3)R1C(1)	101.6 (3)	
P(3)-Cl(1)	3.320 (3)	C(4)-P(3)-P(3)R2C(1)	104.8 (4)	103.9
Cl(1)-P(1)R2H(6)	2.69	P(3)R1C(1)-P(3)-P(3)R2C(1)	105.3 (3)	
Cl(1)-P(3)R2H(6)	2.67	P(1)-C(1)-C(2)	118.0 (6)	
N(1)-P(1)R1H(6)	2.54	C(1)-C(2)-C(3)	115.0 (8)	
N(1)-P(3)R1H(6)	2.51	C(2)-C(3)-P(2)	114.8 (6)	115.2
N(2)-P(2)	3.240 (8)	P(3)-C(4)-C(5)	114.7 (6)	
N(1)-P(2)	3.149 (8)	C(4)-C(5)-C(6)	113.6 (8)	
N(1)-Cl(1)	3.330 (8)	C(5)-C(6)-P(2)	115.3 (6)	
		Cl(2)-C(13)-Cl(3)	112.3 (8)	

Table VIII

Selected Planes in  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ ;  $Ax + By + Cz = D^a$ 

Plane	A	B	C	D	Atoms	Mean dev, Å
1	4.57	3.05	10.55	2.10	Cl(1), P(1), P(2), P(3) <sup>b</sup>	0.077
2	-4.53	-2.28	-11.14	-2.39	P(1), P(2), P(3)	
3	10.62	-1.13	-9.78	-1.48	Rh, N(1), N(2), C(7) <sup>b</sup>	0.038
4	-10.66	0.91	9.61	1.47	Rh, N(1), N(2)	
5	10.51	-1.99	-10.27	-1.69	N(1), N(2), C(7)	
6	11.24	-7.49	-7.38	-0.22	Rh, Cl(1), P(2)	
7	1.72	11.23	-5.47	-2.35	Rh, P(1), P(3)	
8	11.16	-3.32	-9.32	-1.00	C(7), C(8), C(9), C(10), C(11), C(12) <sup>b</sup>	0.009

Distances (Å) of Various Atoms from Selected Planes

Atom	Distance	Atom	Distance	Atom	Distance	Atom	Distance
	Plane 1		Plane 3		Plane 4		Plane 7
Rh	0.220	Rh	0.0002 (7)	C(7)	-0.142	N(1)	0.472
Cl(1)	-0.072 (2)	N(1)	-0.041 (8)				
P(1)	0.075 (2)	N(2)	-0.043 (9)		Plane 5		Plane 8
P(2)	-0.085 (2)	C(7)	0.066 (10)	Rh	0.180	C(7)	-0.011 (9)
P(3)	0.076 (2)	C(8)	-0.084			C(8)	0.008 (12)
		C(9)	-0.018	N(1)	-0.214	C(9)	0.010 (13)
	Plane 2	C(10)	0.183			C(10)	-0.014 (13)
Rh	-0.146	C(11)	0.352			C(11)	0.000 (12)
Cl(1)	0.315	C(12)	0.311			C(12)	0.011 (10)

<sup>a</sup> Triclinic coordinates. <sup>b</sup> Weighted least-squares planes.

atoms is given in Table VIII along with those for other selected planes. The Rh atom is displaced by 0.220 Å above this plane in the direction of the phenyldiazo group. This displacement is less than the corresponding distance in  $[\text{RhLCl}(\text{NO})]^+$ ,<sup>20</sup> 0.255 Å, suggesting that the interaction between the Rh atom and the phenyldiazo group is weaker than the Rh-NO interaction. The Rh-N(1) distance in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ , 1.961 (7) Å, is marginally longer than the Rh-N distance in  $[\text{RhLCl}(\text{NO})]^+$ , 1.909 (15) Å, and is thus supportive of such a conclusion. However, the precision of the two Rh-N distances precludes any strong statement as to the significance of the difference between these two bond lengths.

The most striking feature of the  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  cation is the stereochemical arrangement about the N-N bond of the coordinated phenyldiazo function (Figure 3). The bond angles at the two N atoms, 125.1 (6) and 118.9 (8)° about N(1) and N(2), respectively, and the torsional angle about the N(1)-N(2) bond, 6.4 (6)°, strongly suggest  $sp^2$  hybridization for these two atoms. The bond angle at N(1) is particularly significant in that it is entirely analogous to the arrangement found in certain complexes<sup>3,20</sup> of the nitrosonium cation,  $\text{NO}^+$ . In these compounds the bond angle at the N atom of the coordinated nitrosyl function ( $\sim 120^\circ$ ) provides the basis for the formalistic view of these materials as complexes of  $\text{NO}^-$ . By analogy then, the coordination of the isoelectronic  $\text{N}_2\text{Ph}^+$  cation in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  may be viewed as involving a reduced form of the phenyldiazo function,  $\text{N}_2\text{Ph}^-$ , with the structural details of the Rh-N-N-Ph linkage being rationalized in terms of the valence-bond representation, II. As noted above, the three previous structure determinations of aryldiazo complexes<sup>13,16,17</sup> all reveal an M-N-N angle of *ca.* 180°<sup>34,35</sup> consistent with formulation Ib,  $\text{ArN}_2^+$ . The present results thus represent the first conclusive evidence that the aryldiazonium cation is capable of the same duality in bonding as is the nitrosonium cation.

The N(1)-N(2) distance, 1.172 (9) Å, is intermediate between that expected for a formal N-N double bond, 1.23 Å,<sup>36</sup> and an N-N triple bond, 1.098 Å,<sup>33</sup> suggesting that the formalistic representation II may not be entirely adequate to describe the N-N and M-N-N interactions. Support for this contention is found in the three previously reported structure determinations of aryldiazo complexes<sup>13,16,17</sup> where the N-N bond length varies from 1.14 to 1.23 Å for what must in each case be considered a formal N-N double bond, Ib. A similar situation obtains in nitrosyl complexes<sup>3</sup> leading some authors to suggest<sup>37</sup> that (1) the N-O bond length in these compounds may not be particularly sensitive to bond order and (2) the low precision and high scatter associated with these distances precludes any distinctions based on the N-O bond length. On the basis of the four aryldiazo complexes reported thus far it would appear that such is the case for the N-N bond distance as well.

The Rh-N(1) distance, 1.961 (7) Å, is longer by *ca.* 0.16 Å compared with the M-N distances in the three complexes involving a coordinated  $\text{ArN}_2^+$  function.<sup>13,16,17</sup> The M-N distances in aryldiazo complexes are thus consistent with data on nitrosyl complexes<sup>3</sup> where the increase of *ca.* 0.18 Å in the M-N distance in going from  $\text{NO}^+$  to  $\text{NO}^-$  may be attributed to a decrease in the  $d\pi-\pi^*(\text{NO})$  interaction accompanying the decrease in the M-N-O angle from 180 to 120°.

The N(2)-C(7) distance, 1.445 (11) Å, agrees with that expected for an N-C single bond, 1.47 Å,<sup>33</sup> and is only slightly longer than the corresponding distance in *trans*-azobenzene, 1.41 Å.<sup>36</sup> The C atoms of the phenyl ring of the aryldiazo group are coplanar (Table VIII) to within 0.01 Å. The C-C distances and internal angles of the ring (Table VII) show some variation compared with the accepted values, 1.392 Å and 120°. However, the averaged values, 1.37 (4) Å and 120 (2)°,

for the C-C distance and C-C-C angle, respectively, suggest that these variations are not significant. The random pattern of the variations precludes any interpretation based on reduced (quinoidal) forms for the phenyl ring. The plane of the phenyl ring is slightly (9.6°) twisted with respect to the mean plane of the N=N bond which, for purposes of discussion, is defined (Table VIII) by Rh, N(1), N(2), and C(7). None of the nine atoms comprising the combination of metal atom and apical ligand deviates from this plane by more than 0.35 Å. From a somewhat simplistic point of view then, the complex may be viewed as a substituted (RhLCl) *trans*-phenyldiazene.

This *trans* arrangement about the N=N bond is dictated by stereochemical constraints imposed by the ligand, L, at the base of the tetragonal pyramid. Model building together with geometrical considerations indicate that a *cis* arrangement about the N=N bond is sterically impossible as long as the tetragonal-pyramidal arrangement about the Rh atom remains intact. The mean plane of the N=N bond roughly eclipses the less stereochemically hindered P(2)-Rh-Cl(1) axis (dihedral angle 29.5°). This *ca.* 30° rotation about the Rh-N(1) bond results from nonbonded interactions between lone pairs on the two N atoms and P(2) and Cl(1) in the basal plane. A consideration of these interactions provides a rationale for the structural differences between  $[\text{RhLCl}(\text{NO})]^+$  and  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ .

A comparison of the metrical details of  $[\text{RhLCl}(\text{NO})]^+$  and  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  reveals that the two complex cations are structurally very similar. The dihedral angle in the basal plane of  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  is 87.52 (15)° compared with the symmetry ( $C_s$ )-constrained value, 90°, in  $[\text{RhLCl}(\text{NO})]^+$ . The corresponding Rh-X distances (X = Cl, P) in the two complexes are comparable as are the conformational details of the ligand, L (*vide infra*). The N atom at the apex of the tetragonal pyramid lies roughly along the line of intersection of the two dihedral planes at the base of the pyramid: 0.52 (2) Å off-axis in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  compared with 0.33 (2) Å off-axis in  $[\text{RhLCl}(\text{NO})]^+$ . The major differences that exist occur in the interatomic angles within the coordination spheres of the two complexes. The P(2)-Rh-Cl angle increases from 159.30 (15)° in the NO complex to 165.18 (8)° in the  $\text{N}_2\text{Ph}$  complex. There is a corresponding decrease in the N(apical)-Rh-Cl angle from 104.3 (5)° (NO) to 98.9 (2)° ( $\text{N}_2\text{Ph}$ ). However, the N(apical)-Rh-P(2) angles are essentially identical, 96.43 (5)° in  $[\text{RhLCl}(\text{NO})]^+$  compared with 95.8 (2)° in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ , as are the remaining angles within the coordination sphere. It would therefore appear that the position of the chloro ligand with respect to the remainder of the basal plane (P(1), P(2), P(3)) is variable in these complexes. Such a result is not unexpected in view of the constraints imposed on the ligand, L, by chelation. Support for this conclusion is found in a comparison of the positions of the chloro ligands relative to the plane defined by the three P atoms in RhLCl,  $[\text{RhLCl}(\text{NO})]^+$ , and  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ . These distances are -0.304 (5),<sup>38</sup> -0.461 (5), and -0.310 (4) Å, respectively, for the three complexes. The chloro ligand in  $[\text{RhLCl}(\text{NO})]^+$  thus lies *ca.* 0.15 Å further below the P(1), P(2), P(3) plane than the chloro ligands either in the parent complex or in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ . This movement of the chloro ligand in  $[\text{RhLCl}(\text{NO})]^+$  has occurred in response to nonbonded repulsion between itself and the lone-pair density localized on the apical N atom. The imposed  $C_s$  symmetry of the NO complex requires that the major component of this lone-pair density lie in the dihedral plane defined by P(2), Rh, and Cl. The N(apical)-Cl distance in  $[\text{RhLCl}(\text{NO})]^+$  is 3.42 (2) Å and, as noted above, the N(apical)-Rh-Cl angle is 104.3 (5)°. If this angle were 98.9°, as found in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ , the N(apical)-Cl distance would be 3.30 Å which is both the sum of the van der Waals radii for N and Cl<sup>39</sup> and the

**Table IX.** Conformational Angles in the Chelate Rings of  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ 

Atoms	Angle, deg	Atoms	Angle, deg
Rh-P(1)-C(1)-C(2)	-50.3 (8)	Rh-P(3)-C(4)-C(5)	+57.1 (7)
P(1)-C(1)-C(2)-C(3)	+63.5 (10)	P(3)-C(4)-C(5)-C(6)	-76.7 (9)
C(1)-C(2)-C(3)-P(2)	-69.9 (9)	C(4)-C(5)-C(6)-P(2)	+70.5 (9)
C(2)-C(3)-P(2)-Rh	+64.1 (7)	C(5)-C(6)-P(2)-Rh	-48.5 (8)
C(3)-P(2)-Rh-P(1)	-41.8 (4)	C(6)-P(2)-Rh-P(3)	+27.8 (4)
P(2)-Rh-P(1)-C(1)	+35.7 (3)	P(2)-Rh-P(3)-C(4)	-30.6 (3)

N(apical)-Cl distance in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ . In  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  this lone-pair interaction is avoided by a 30.4 (9) $^\circ$  rotation of the plane containing the N(apical) lone pair (Rh, N(1), N(2)) relative to the P(2)-Rh-Cl(1) plane allowing the Cl atom to approach the P(1), P(2), P(3) plane to the same extent as in the parent complex and reducing the N(1)-Cl(1) distance to 3.330 (8) Å.

A similar situation is found in comparing the angles at the apical N atoms of the NO (131 (1) $^\circ$ ) and N<sub>2</sub>Ph (125.1 (6) $^\circ$ ) complexes. In both compounds the N(apical)-Rh-P(2) angle is held fixed by chelating constraints. In  $[\text{RhLCl}(\text{NO})]^+$  the imposed mirror symmetry causes the nonbonded repulsion between P(2) and the lone-pair density localized on the O atom to be relieved by an increase in the Rh-N-O angle from the expected 120 $^\circ$  to ca. 131 $^\circ$ . In  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  the corresponding interaction between P(2) and the lone-pair density on N(2) is relieved by a 26 (1) $^\circ$  rotation of the plane containing the N(2) lone pair (N(1), N(2), C(7)) relative to the P(2)-Rh-Cl(1) plane. This rotation allows the Rh-N(1)-N(2) angle to approach more closely the expected value, 120 $^\circ$ .

The movement of the chloro ligand relative to the P(1), P(2), P(3) plane is not without constraint. Short intramolecular contacts between the Cl atom and H atoms bonded to the two terminal phenyl rings lying below the basal plane (Figure 2) prevent uninhibited movement of the Cl atom below the basal plane. These contact distances (Table VII) are the same as those found in RhLCl and  $[\text{RhLCl}(\text{NO})]^+$  suggesting that small changes in the orientation of the phenyl rings in the name of packing efficiency serve to keep the Cl-H contacts roughly constant. There is one additional short intramolecular contact in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$ . It occurs between the Rh atom and P(2)R1H(2) at 2.82 Å and effectively blocks the sixth coordination site of the Rh atom. This contact is identical with those found in RhLCl and  $[\text{RhLCl}(\text{NO})]^+$ .

**Structural Details of the Ligand, L.** The overall conformation of the triphosphine ligand, L, is the same as that found in the nitrosyl complex,  $[\text{RhLCl}(\text{NO})]^+$ . The Rh-P distances (Table VII) show an increase, relative to those of the parent complex, RhLCl, that is comparable to that found in the NO complex. This increase as well as the pattern of Rh-P distances has been discussed previously.<sup>20</sup> The mean bite distance for the chelate rings in  $[\text{RhLCl}(\text{N}_2\text{Ph})]^+$  is the same as that found in  $[\text{RhLCl}(\text{NO})]^+$ . The mean P-C(phenyl) and P-C(alkyl) distances, 1.825 (9) and 1.834 (10) Å, respectively, are well within the expected range. The mean C-C distance in the propyl chains is 1.52 (1) Å. The average Rh-P-C and C-P-C angles within the ligand (Table VII) show a ca. 5 $^\circ$  expansion and contraction, respectively, relative to the tetrahedral value. This effect has previously been noted in triphenylphosphine complexes.<sup>40</sup> The mean C-C-C angle in the propyl chains is 115.2 $^\circ$ . As in the parent and nitrosyl complexes the propyl chains linking the P atoms adopt a gauche conformation about the C-C bonds. Each six-membered chelate ring exhibits the chair conformation. The two independent chelate rings are approximate mirror images. This result is to be expected since the closely related NO complex has imposed mirror symmetry relating the two rings. This approximate mirror symmetry is reflected in the correspondence of the conformational angles for the two rings (Table IX).

## Conclusions

The reaction of the phenyldiazonium cation, Ph-N≡N<sup>+</sup>, with the four-coordinate Rh(I) complex, RhLCl, has been shown to lead to the formation of a stable, discrete five-coordinate tetragonal-pyramidal cation in which the phenyldiazo function occupies the apical coordination site. Consideration of the metrical details of the Rh-N-N-Ph linkage definitely establishes that Ph-N≡N<sup>+</sup> is capable of the same duality of bonding and function upon coordination to a transition metal as is NO<sup>+</sup>. The close similarity between the Rh-N-N-Ph linkage in the present complex and the Rh-N-O linkage in  $[\text{RhLCl}(\text{NO})]^+$  suggests that the formation of the complex may formally be viewed as resulting from the oxidative addition of Ph-N≡N<sup>+</sup> to RhLCl yielding a cationic complex of Rh(III) and PhN<sub>2</sub><sup>-</sup>. A comparison of the details of these two linkages leads to a rationale for the distortion of the angle at the apical N atom in the NO<sup>-</sup> and PhN<sub>2</sub><sup>-</sup> complexes from the expected 120 $^\circ$  value.

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**Registry No.**  $[\text{RhLCl}(\text{N}_2\text{Ph})][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ , 53042-54-9.

**Supplementary Material Available.** A listing of structure amplitudes and Table V showing the idealized positions for the hydrogen atoms of  $[\text{Rh}(\text{C}_6\text{H}_5\text{P}((\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2)_2)\text{Cl}(\text{N}_2\text{C}_6\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$  will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number AIC405790.

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## New Complexes of Pentaamminechromium(III) with Oxalate, Glycinate, Sulfate, and Iodate as Ligands. Loss of Ammonia from Chromium(III)-Ammine Complexes

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Complexes of general formula  $[\text{Cr}(\text{NH}_3)_5\text{X}]^{(3-n)+}$  with  $\text{X}^{n-} = \text{HC}_2\text{O}_4^-$ ,  $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{IO}_3^-$  have been prepared as perchlorate and, in the case of  $\text{X}^{n-} = \text{IO}_3^-$ , perchlorate-iodate salts. Elemental analyses, uv-visible and ir spectra, and charge determinations have been used to characterize the complexes. Kinetic studies are also reported and support formulations in which  $\text{X}^{n-}$  is monodentate. It has not been possible to repeat preparations of iodato complexes  $[\text{Co}(\text{NH}_3)_5\text{IO}_3]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{IO}_3]^{2+}$  previously described, and data obtained suggest that earlier assignments are incorrect. To our knowledge no other metal-pentaammine complexes with iodate as a ligand have been reported. The relative effectiveness of different  $\text{X}^{n-}$  ligands on the rate of aquation of ammonia in these and other pentaamminechromium(III) complexes is considered.

Whereas the vast majority of cobalt(III)-ammine complexes are extremely inert to loss of ammonia, the situation with chromium(III) is less clear-cut.<sup>1</sup> Reactions which  $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]^{2+}$ ,<sup>2</sup>  $[\text{Cr}(\text{NH}_3)_5\text{O}_2\text{CR}]^{2+}$  (R =  $\text{CHCl}_2$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CH}_3$ ),<sup>3</sup> and other chromium(III) complexes<sup>1</sup> undergo suggest that ammonia is much more readily displaced. Pentaamminechromium(III) complexes ( $\text{X}^{n-} = \text{HC}_2\text{O}_4^-$ ,  $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$ , and  $\text{SO}_4^{2-}$ ), the cobalt(III) analogs of which are readily prepared, have not previously been isolated. Procedures for the preparation of these complexes are reported in this paper. At the same time because of its relevance to the efficiency of procedures described, processes involving ammonia loss are considered. Different categories of reaction are defined and possible mechanisms are discussed.

The preparation of the iodato complex falls in a different category in that ammonia loss is not significant. Duval<sup>4</sup> and Lobanov<sup>5</sup> have previously reported the preparation of iodato complexes of cobalt(III). Since the procedures which they used were of possible relevance to the preparation of  $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ , attempts were made to repeat their work.

### Experimental Section

Samples of  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$  were prepared<sup>6</sup> and converted to the perchlorate salt using standard procedures. The complex *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$  was obtained by the method of Hoppenjans and Hunt.<sup>7</sup>

**Preparation of Pentaammineoxalatochromium(III) Perchlorate.** Oxalic acid, AR (8 g), was dissolved in a 95:5 methanol (AR)-water mixture (200 ml), and  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  (1 g) was added. The mixture was maintained at ca. 20° for 5-6 hr, after which  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  crystals were removed by filtration. The solution was concentrated by rotary evaporation at 35-40° and a mixture of  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ,  $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}]^{2+}$ , and  $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^{+}$  was precipitated by the addition of 1:1 ethanol-ether and cooling in ice. The orange precipitate was dissolved in 0.3 M  $\text{HClO}_4$  also at

0° which was then passed down an ice-cooled Dowex 50W-X2 (100-200 mesh) resin column (12 cm × 1 cm). Three bands were observed and the first (red) band, which was later identified as  $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^{+}$ , eluted with a solution containing 0.3 M  $\text{LiClO}_4$  and 0.2 M  $\text{HClO}_4$ . Under these conditions one of the two remaining bands (both of which are orange) moved about 2 cm down the column. Using an eluent mixture of 0.8 M  $\text{LiClO}_4$ -0.2 M  $\text{HClO}_4$  both orange bands were eluted, with a separation of about 5 cm between the two bands at the end of the elution. The solution containing the first orange band was cooled to 0° when crystals were obtained. The ir spectrum of these is illustrated in Figure 1. The elution characteristics of the complex on the ion-exchange column, together with the ammonia to chromium ratio of 4.9:1, as determined using micro Kjeldahl and chromate analyses, indicate a formulation  $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}](\text{ClO}_4)_2$ . The second orange fraction obtained from the column gave a visible spectrum in agreement with that of  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  and corresponded to the unreacted starting material.

**Preparation of Pentaammineglycinatochromium(III) Perchlorate.** Glycine, AR (9 g), was dissolved in ca. 30 ml of 1 M  $\text{HClO}_4$  to give a final pH of ca. 3.0. The solution was then warmed to 50° and  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  (5 g) was added, the temperature being maintained at 50° for 10 min. By the addition of suitable amounts of  $\text{NaClO}_4$  and subsequent cooling it was possible to crystallize what later proved to be a mixture of  $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  and  $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$ , leaving a red supernatant liquid. The mixed crystals were filtered off, washed with alcohol and ether, and then dissolved in 500 ml of methanol (AR) with stirring. The glycinate component of the mixture was soluble and readily separated from the insoluble aquo species. The methanolic solution was then concentrated by rotary evaporation and the glycinato product precipitated by the addition of a 1:1 alcohol-ether mixture. The orange product was recrystallized three times from 20-ml quantities of 1 M  $\text{HClO}_4$ . *Anal.* Calcd for  $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$ : C, 4.71; H, 3.94; N, 16.48; Cl, 20.8; Cr, 10.2. Found: C, 4.7; H, 4.2; N, 16.2; Cl, 20.65; Cr, 10.2.

**Preparation of Tetraammineaquoglycinatochromium(III) Perchlorate.** This complex was prepared in solution by treating