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Coordination of the Arylazo Group. Molecular Structure of Trichloro(*p*-tolylazo)bis(triphenylphosphine)ruthenium(II)-Acetone, $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2 \cdot \text{Me}_2\text{CO}$

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The arylazo complex $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ has been synthesized in high yield and its crystal and molecular structure determined from three-dimensional X-ray data collected by the θ - 2θ scan technique with a scintillation detector. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 12.503$ (8), $b = 18.569$ (13), $c = 18.545$ (9) Å, $\beta = 92.45$ (3)°, and $V = 4302$ Å³. The experimental and calculated densities of 1.44 (3) and 1.403 g/cm³ agree for $Z = 4$ with one molecule of acetone per molecule of complex. The molecular structure was determined by standard Patterson and Fourier methods and has been refined by a least-squares procedure to a final R factor of 0.045 for 2478 reflections having $F_o \geq 6\sigma(F_o)$. The structure of the complex is essentially octahedral with the two triphenylphosphine ligands in trans positions. The *p*-tolylazo group coordinates in a linear manner with a Ru-N distance of 1.796 (9) Å and a Ru-N-N bond angle of 171.2 (9)°. The short Ru-N distance is only slightly longer than corresponding values reported for linearly coordinated nitrosyls of ruthenium, indicating a strong π interaction between the arylazo group and the metal ion in the present complex. The linearly coordinated arylazo group can thus be considered formalistically as ArN_2^+ or a three-electron donor in analogy with the bonding of NO^+ . Other important bond parameters for the structure are as follows: N-N, 1.144 (10) Å; Ru-P, 2.434 (4) Å; Ru-Cl, 2.388 (3) Å; N-N-C, 135.9 (11)°.

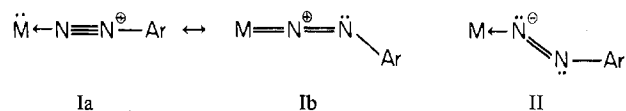
Introduction

In 1967, Parshall¹ proposed a model for the enzymatic reduction of dinitrogen based on the interaction of aryldiazonium cations with a transition metal hydride complex. The aryldiazonium cations were viewed by Parshall as convenient analogs to an initially formed metal-dinitrogen complex, and the activation process was seen as the insertion of the coordinated N_2 functional group into the metal-hydride bond of a different metal center. The use of aryldiazonium cations in this model system and the fact that these compounds are isoelectronic with NO^+ has stimulated great interest in the chemistry of aryldiazonium complexes and their relationship to analogous nitrosyl systems.

During the last few years, nitrosyl complexes of the group VIII elements have been vigorously studied.²⁻²⁵ X-Ray

structure determinations¹¹⁻²⁵ have shown that nitric oxide coordinates to transition metal ions in primarily one of two ways, either as formally NO^+ with a linear M-NO group or as NO^- with a trigonally hybridized N atom and a bent M-NO arrangement. These two predominant types of nitrosyl coordination have been interpreted in terms of the amphoteric nature of nitrosyl as a ligand.^{3,11,15,17} In the linear mode of bonding, NO^+ functions as a Lewis base or electron pair donor (and π acceptor), whereas in the bent arrangement it acts as a Lewis acid or electron pair acceptor. The Lewis acid behavior of NO^+ is most notable in discussing the bent nitrosyl groups in complexes such as $\text{IrCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2^+$ ¹¹ and $\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2^+$ ²¹ which are formed by the reaction of NO^+ with the parent d^8 metal complex. In these cases, the nitrosyl group undergoes a formal two-electron reduction upon coordination with consequent bond order lowering and rehybridization of the nitrogen atom.

The isoelectronic nature of NO^+ and ArN_2^+ leads one to speculate that the coordinated aryldiazonium cation may also exhibit a duality of bonding modes characterized by linear and bent M-N-N structural units. These stereochemical arrangements correspond to the bonding schemes portrayed in structures I and II with the formal charges as shown.²⁶



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(21) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972); *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

(22) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1094 (1972).

(23) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 1420 (1972).

(24) M. O. Visscher and K. G. Caulton, *J. Amer. Chem. Soc.*, **94**, 5923 (1972).

(25) R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpont, J. Reed, and A. J. Schultz, *J. Amer. Chem. Soc.*, **94**, 6240 (1972).

(26) The assignment of formal charges can sometimes be absurdly confusing. In the present examples, the M-N σ bonds are dative covalent and the electron pairs contained therein are assigned to the donor N atoms in computing their formal charges. This assignment is in accord with the normal oxidation state formalism used for metal complexes.

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(1) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967).

(2) For a review of nitrosyl complexes through 1965, see B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, **7**, 277 (1966).

(3) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969).

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(9) S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3068 (1971).

(10) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971).

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D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

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(16) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).

(17) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

(18) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, **10**, 1043 (1971).

(On the basis of the structural data outlined below, Ib is clearly more important than Ia in describing the linear mode of bonding.) Once coordinated, the ArN_2 ligands are best referred to as arylazo groups. The analogy of ArN_2^+ and NO^+ , together with use of the former in nitrogenase model systems, has also fostered the postulation^{1,27} of an alternative mechanism for the activation of dinitrogen based on structure II in which bond order lowering and rehybridization of both nitrogen atoms are achieved upon coordination. The relevance of this proposal, however, must await more detailed structural and mechanistic information concerning the enzyme system. Nevertheless, because of their inherently interesting chemistry, investigations into the coordinating properties of aryl diazonium cations continue.

In a recent study, McCleverty and Whiteley²⁸ reported a series of ruthenium arylazo complexes in which it seemed probable that the arylazo ligand was exhibiting both types of coordination. These complexes were prepared from a series of reactions between $\text{RuXCl}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{H}$) and ArN_2^+ . We have developed a high yield synthesis of one member of this series, $\text{RuCl}_3(\text{N}_2\text{Ar})(\text{PPh}_3)_2$, and we report herein its structure determination. The potential importance of this complex to the other arylazo complexes is best appreciated by noting that its nitrosyl analog, $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$,²⁹ is the parent compound of most ruthenium nitrosyl tertiary phosphine complexes.

To date, there have been relatively few structure determinations of arylazo complexes.³⁰⁻³³ In $\text{ReCl}_2(\text{N}_2\text{C}_6\text{H}_5)(\text{PMe}_2\text{-Ph})_3$ ³⁰ and $(\text{HB}(\text{pz})_3)\text{Mo}(\text{CO})_2(\text{N}_2\text{C}_6\text{H}_5)$,³¹ the M-N-N unit is found to be linear with a relatively short M-N bond, whereas in $\text{IrCl}(\text{NHNC}_6\text{H}_3\text{F})(\text{CO})(\text{PPh}_3)_2$,³³ the Ir-N-N unit is required to be bent with the three atoms forming part of a five-membered chelate ring. In a related compound two aryl diazonium cations couple in the presence of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ to form a coordinated tetrazene moiety.³⁴ In studying the ruthenium arylazo complexes, we seek to elucidate the structural systematics and chemistry of the coordinated arylazo group and to determine if its complexes possess the same interesting properties as the corresponding nitrosyls.

Experimental Section

Preparation of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$. A 0.7-g sample of $\text{RuCl}_2(\text{PPh}_3)_3$ ³⁵ was suspended in a 3:1 solution of previously degassed ethanol-acetone under N_2 . To this suspension 0.7 g of $(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{BF}_4)$ was added, followed by 0.5 g of LiCl dissolved in 20 ml of ethanol. The reaction mixture was then refluxed for 2 hr, cooled to room temperature, and filtered. The precipitate was washed with H_2O and ether and then dried under vacuum. The product is a light brown powder obtained in 90% yield. Recrystallization from acetone-hexane affords a brown crystalline product. The infrared spectrum of this product is identical with that of the material used in the structure determination.

Anal. Calcd for $\text{C}_{33}\text{H}_{37}\text{Cl}_3\text{N}_2\text{P}_3\text{Ru}\cdot\text{C}_3\text{H}_6\text{O}$: C, 60.77; H, 4.77; Cl, 11.70; N, 3.08; P, 6.81. Found: C, 60.94; H, 4.62; Cl, 11.80; N, 3.02; P, 7.03.

(27) A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *Nature (London)*, **235**, 42 (1972).

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Collection and Reduction of the X-Ray Data. The synthesis described above was devised after the structure of the complex was determined. The crystals of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ used for the structure study were obtained from successive recrystallizations of the bis-arylazo complex $[\text{RuCl}(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})_2(\text{PPh}_3)_2](\text{BF}_4)$.²⁸ These crystallizations were performed using halogenated hydrocarbon solvents together with acetone. From the results it appears that the title complex is a decomposition product of the bis-arylazo complex in the presence of possible halide ion donors. Single-crystal precession photographs of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ showed the complex to crystallize in the monoclinic system. Observed systematic extinctions of $h0l$ for $l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ are consistent with the monoclinic space group $P2_1/c$ (No. 14, C_{2h}^2).³⁶ The unit cell constants were determined at ambient room temperature from a least-squares refinement³⁷ of the angular settings of 12 diffractometer-centered reflections using $\text{Mo K}\alpha$ radiation (λ 0.7107 Å) and are found to be $a = 12.503$ (8), $b = 18.569$ (13), $c = 18.545$ (9) Å, $\beta = 92.45$ (3)°, and $V = 4302$ Å³. An observed density of 1.44 (3) g/cm³ obtained by the flotation method in methylene chloride-chloroform solution agrees favorably with a value of 1.403 g/cm³ calculated for the monoacetone solvate of the complex with four formula units per unit cell ($Z = 4$).

The crystal used for the intensity data collection was of approximate dimensions $0.22 \times 0.17 \times 0.16$ mm (the longest dimension being the a^* direction). The crystal was mounted along the c^* direction and aligned accurately on a precession camera. After the crystal was transferred to the diffractometer, its mosaic spread was determined from open-counter, narrow-source ω scans³⁸ through several strong reflections and found to have an average value of 0.07°. The intensity data were collected by the θ - 2θ scan technique using a Picker FACS-DOS diffractometer equipped with a graphite monochromator. $\text{Mo K}\alpha$ radiation was employed with a 2.5° takeoff angle and a counter opening of 4×4 mm. Each reflection was measured from -0.7 to $+0.7^\circ$ of the calculated 2θ value for the reflection at a scan rate of $1^\circ/\text{min}$. The background was counted for 10 sec at each end of the scan range. The maximum 2θ value for the reflections which were measured was 45° . The intensities of three strong reflections were measured after every 100 reflections to check on crystal and electronic stability. No systematic variation of these standards was observed, and no standard deviated by more than 2.5% from its mean value.

The intensities of 5142 independent reflections were measured and corrected for the usual Lorentz and polarization effects to yield a set of F_o values where F_o is the observed structure factor amplitude. Of the 5142 independent reflections measured, 2478 were assumed to be statistically reliable, having $F_o \geq 6\sigma(F_o)$. The standard deviations $\sigma(F_o)$ were estimated according to the formula

$$\sigma(F_o) = (2F_o)^{-1}(Lp)^{-1}(CT + r^2(BG))^{1/2} + 0.03F_o$$

where CT is the total count, BG is the sum of the background counts, r is the ratio of scan time to the total background counting time, and Lp is the Lorentz-polarization factor. The term $0.03F_o$ is included in the estimation of $\sigma(F_o)$ because the Picker FACS-DOS system does not include in its calculation of $\sigma(F_o^2)$ the uncertainty term pI where I is the net intensity and p is a factor in the range 0.02-0.05. The criterion $F_o \geq 6\sigma(F_o)$ is thus equivalent to $F_o^2 \geq 3.7\sigma(F_o^2)$ based solely on counting statistics. The absorption coefficient was calculated to be 6.58 cm^{-1} and therefore no absorption correction was performed.

Solution and Refinement of the Structure. The position of the Ru atom was determined from a three-dimensional Patterson function map.³⁷ A difference Fourier map based on phases obtained from the Ru atom contribution revealed the positions of five heavy atoms, which were taken to be the phosphorus and chlorine atoms, and all of the carbon atoms of the triphenylphosphine ligands. The six phenyl rings of the phosphine ligands were treated as groups in all refinement procedures as outlined below. The positional and iso-

(36) "International Tables of X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 99.

(37) The Picker FACS-DOS refinement and setting program was performed on a PDP-8/E computer. All other computing for this study was performed on Brown University's IBM 360/67 computer. The programs used were local versions of the Busing-Levy ORFLS least-squares program, the Ibers-Doedens group refinement least-squares program, the Zalkin FORDAP Fourier program, the Busing-Martin-Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program.

(38) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

Table I. Final Positional and Thermal Parameters for $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2 \cdot \text{Me}_2\text{CO}$

Atom ^a	x^b	y^b	z^b	B^c
Ru	0.08463 (8) ^d	0.02527 (5)	0.22307 (5)	<i>e</i>
Cl(1)	0.0619 (2)	-0.0306 (2)	0.1072 (2)	<i>e</i>
Cl(2)	0.1525 (2)	-0.0804 (2)	0.2820 (2)	<i>e</i>
Cl(3)	0.0984 (2)	0.0837 (2)	0.3377 (2)	<i>e</i>
P(1)	-0.0978 (2)	-0.0112 (2)	0.2448 (2)	<i>e</i>
P(2)	0.2658 (2)	0.0538 (2)	0.1888 (2)	<i>e</i>
N(1)	0.0375 (7)	0.1088 (5)	0.1847 (5)	<i>e</i>
N(2)	0.0093 (8)	0.1655 (5)	0.1690 (5)	<i>e</i>
C(1)	-0.0296 (9)	0.1994 (6)	0.1055 (6)	3.6 (2)
C(2)	-0.0353 (10)	0.1640 (7)	0.0412 (7)	4.3 (3)
C(3)	-0.0758 (10)	0.2000 (7)	-0.0214 (7)	4.7 (3)
C(4)	-0.1087 (9)	0.2724 (6)	-0.0171 (7)	4.7 (3)
C(5)	-0.0978 (10)	0.3073 (7)	0.0478 (7)	4.6 (3)
C(6)	-0.0608 (11)	0.2719 (7)	0.1111 (7)	5.0 (3)
C(7)	-0.1489 (11)	0.3110 (7)	-0.0863 (8)	6.4 (3)
H(2)	-0.014 (11)	0.130 (7)	0.039 (7)	6.0 ^f
H(3)	-0.056 (10)	0.170 (7)	-0.072 (7)	6.0
H(5)	-0.140 (10)	0.349 (7)	0.061 (7)	6.0
H(6)	-0.051 (10)	0.303 (7)	0.157 (7)	6.0
Ac(1)	-0.463 (3)	0.346 (2)	0.115 (2)	22.6 (12)
Ac(2)	-0.400 (2)	0.376 (2)	0.068 (2)	16.5 (10)
Ac(3)	-0.484 (2)	0.375 (1)	0.180 (2)	16.9 (9)
Ac(4)	-0.480 (3)	0.288 (2)	0.078 (2)	21.9 (12)

Atom	Anisotropic thermal parameters ^g						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B^c
Ru	54 (1)	20 (0)	19 (0)	1 (0)	3 (0)	2 (0)	
Cl(1)	87 (3)	30 (1)	25 (1)	-2 (2)	5 (1)	-3 (1)	
Cl(2)	72 (3)	28 (1)	36 (1)	2 (1)	3 (1)	7 (1)	
Cl(3)	83 (3)	31 (1)	26 (1)	-5 (1)	5 (1)	-1 (1)	
P(1)	57 (3)	22 (1)	21 (1)	0 (1)	3 (1)	1 (1)	
P(2)	56 (3)	26 (1)	23 (1)	-1 (1)	7 (1)	1 (1)	
N(1)	49 (8)	24 (4)	29 (4)	-1 (4)	-4 (4)	5 (3)	
N(2)	76 (9)	23 (4)	37 (4)	8 (5)	2 (5)	5 (3)	

Group	x_c^h	y_c	z_c	ϕ	θ	ρ	B^c
P1R(1)	-0.1808 (4)	-0.1697 (3)	0.1976 (2)	1.256 (4)	-2.991 (4)	0.226 (4)	0.1 (1) ⁱ
P1R(2)	-0.1777 (4)	-0.0194 (2)	0.4076 (3)	-1.951 (5)	3.390 (4)	-1.781 (5)	0.1 (1)
P1R(3)	-0.2446 (4)	0.0969 (3)	0.1487 (3)	-2.042 (9)	-2.107 (5)	-0.851 (9)	0.1 (1)
P2R(1)	0.4089 (4)	-0.0695 (3)	0.1156 (3)	2.337 (4)	-2.973 (5)	0.484 (5)	0.0 (1)
P2R(2)	0.4306 (4)	0.1144 (3)	0.3131 (3)	2.569 (6)	-2.414 (5)	-1.215 (6)	-0.1 (1)
P2R(3)	0.2408 (4)	0.1775 (3)	0.0679 (3)	0.047 (7)	-2.333 (4)	1.458 (7)	-0.1 (1)

^a In the labeling scheme, the number in parentheses of the hydrogen atoms refers to the carbon atom of the tolylazo group to which it is bonded. The atoms in the disordered acetone molecule are designated by Ac (see the text for further discussion). ^b x, y, z are in fractional coordinates. ^c Isotropic thermal parameters in \AA^2 . ^d Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure. ^e Atoms refined anisotropically. ^f Hydrogen thermal parameters were not refined. ^g The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hkl\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic thermal parameters given are $\times 10^4$. ^h x_c, y_c, z_c are the fractional coordinates of the rigid-group centers. The angles ϕ, θ, ρ have been previously defined: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 771 (1965). ⁱ Individual carbon atoms were also assigned variable isotropic thermal parameters (see Table II), although they and the group parameters were never refined on the same cycle. The net effect of refining the group thermal parameter in addition to the individual isotropic temperature factors for the C atoms is to obtain a refined overall B for the H atoms of each group. The hydrogen atoms were included in the group treatment of each phenyl ring.

tropic thermal parameters of the six nongroup atoms and the positional parameters of the phenyl rings, together with the individual group temperature factors assigned to them, were refined through two cycles of least squares. The subsequent difference Fourier map revealed the positions of all of the atoms of the *p*-tolylazo ligand.

Several more cycles of least-squares refinement and a fourth difference Fourier map revealed a cluster of peaks which were refined as a disordered acetone molecule. Various attempts were made to construct models for the disordered solvent molecule by refining partial atoms independently or by imposing rigid-group geometries. However, all of these attempts resulted in either unreasonable bond distances and angles or extremely high temperature factors. Refinement of simply three carbon atoms and one oxygen atom in several orientations led to very long carbon-oxygen bond lengths. Therefore, four carbon atoms were placed at the best positions from a previous disordered model and refined for one cycle. The peaks from the difference Fourier map which led to the choice of solvent molecule positions ranged from 1.20 to 0.85 $e/\text{\AA}^3$ as compared with a value of 1.29 $e/\text{\AA}^3$ for the lowest density C atom in the rest of the structure. It does not appear that the model can be improved in a meaningful way and further attempts to do so do not justify the cost.

The trial structure was refined using a least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were assigned as $\sigma(F_o)^{-2}$. In these calculations, the neutral atom

scattering factors for the nonhydrogen atoms were taken from the report by Cromer and Waber.³⁹ The hydrogen atom scattering factor was that of Stewart, *et al.*⁴⁰ The effects of anomalous scattering were included in the calculated structure factors with values of $\Delta f'$ and $\Delta f''$ for Ru, Cl, and P taken from Cromer's tabulation.⁴¹ The phenyl rings of the triphenylphosphine ligands were treated as rigid groups of D_{6h} symmetry (C-C, 1.392 \AA ; C-H, 0.95 \AA) using the program BUGLES, a local version of the Ibers-Doedens group least-squares program.³⁷ Only those reflections with $F_o \geq 6\sigma(F_o)$ were included in the refinement procedure and in the calculation of discrepancy indices R ($=\Sigma |F_o| - |F_c| / \Sigma |F_o|$) and R' ($=\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2$)^{1/2}.

The Ru, Cl, P, and N atoms were assigned anisotropic thermal parameters, with all other atoms, group and nongroup, being restricted to isotropic thermal motion. This refinement converged to final R and R' factors of 0.045 and 0.061 for the 2478 reflections having $F_o \geq 6\sigma(F_o)$. The final standard deviation of an observation of unit weight is 0.85, indicating that the weights employed may have been underesti-

(39) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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

(41) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table II. Derived Positional and Isotropic Thermal Parameters for Group Atoms

Group atom	x	y	z	B, Å ²	Group atom	x	y	z	B, Å ²
P1R1C(1)	-0.1436 (6)	-0.1010 (3)	0.2153 (4)	3.2 (3) ^a	P2R1C(1)	0.3468 (6)	-0.0176 (4)	0.1483 (4)	4.0 (3)
P1R1C(2)	-0.0715 (4)	-0.1553 (4)	0.1993 (4)	3.9 (3)	P2R1C(2)	0.4464 (6)	0.0008 (3)	0.1230 (4)	5.7 (4)
P1R1C(3)	-0.1087 (5)	-0.2240 (3)	0.1816 (4)	4.4 (4)	P2R1C(3)	0.5084 (5)	-0.0511 (4)	0.0904 (4)	6.5 (5)
P1R1C(4)	-0.2180 (6)	-0.2384 (3)	0.1799 (4)	4.5 (4)	P2R1C(4)	0.4709 (6)	-0.1214 (4)	0.0830 (4)	5.4 (4)
P1R1C(5)	-0.2901 (4)	-0.1842 (4)	0.1958 (4)	4.7 (4)	P2R1C(5)	0.3713 (7)	-0.1398 (3)	0.1082 (4)	6.1 (4)
P1R1C(6)	-0.2529 (5)	-0.1155 (3)	0.2135 (4)	4.0 (4)	P2R1C(6)	0.3093 (5)	-0.0879 (4)	0.1409 (4)	4.3 (4)
P1R1H(2)	0.0030 (4)	-0.1452 (5)	0.2006 (6)	6.0	P2R1H(2)	0.4717 (9)	0.0488 (4)	0.1282 (6)	6.0
P1R1H(3)	-0.0598 (7)	-0.2611 (4)	0.1707 (6)	6.0	P2R1H(3)	0.5765 (6)	-0.0388 (6)	0.0731 (6)	6.0
P1R1H(4)	-0.2434 (8)	-0.2853 (3)	0.1678 (6)	6.0	P2R1H(4)	0.5133 (9)	-0.1568 (5)	0.0607 (6)	6.0
P1R1H(5)	-0.3646 (4)	-0.1943 (6)	0.1946 (6)	6.0	P2R1H(5)	0.3461 (9)	-0.1878 (3)	0.1031 (6)	6.0
P1R1H(6)	-0.3018 (7)	-0.0784 (4)	0.2245 (6)	6.0	P2R1H(6)	0.2413 (5)	-0.1002 (6)	0.1582 (6)	6.0
P1R2C(1)	-0.1441 (6)	-0.0115 (4)	0.3375 (3)	2.9 (3)	P2R2C(1)	0.3603 (7)	0.0893 (5)	0.2586 (4)	4.0 (4)
P1R2C(2)	-0.2477 (5)	0.0079 (4)	0.3540 (4)	4.8 (4)	P2R2C(2)	0.4345 (6)	0.1425 (4)	0.2438 (3)	5.0 (4)
P1R2C(3)	-0.2813 (5)	0.0000 (5)	0.4242 (5)	6.3 (5)	P2R2C(3)	0.5048 (7)	0.1677 (5)	0.2983 (5)	6.0 (4)
P1R2C(4)	-0.2112 (7)	-0.0272 (4)	0.4778 (3)	5.8 (4)	P2R2C(4)	0.5009 (7)	0.1395 (6)	0.3677 (4)	6.2 (4)
P1R2C(5)	-0.1076 (6)	-0.0466 (4)	0.4612 (3)	5.0 (4)	P2R2C(5)	0.4267 (6)	0.0862 (4)	0.3825 (3)	7.0 (4)
P1R2C(6)	-0.0741 (5)	-0.0388 (4)	0.3910 (4)	3.8 (3)	P2R2C(6)	0.3564 (7)	0.0611 (5)	0.3280 (4)	4.4 (4)
P1R2H(2)	-0.2953 (7)	0.0264 (5)	0.3173 (5)	6.0	P2R2H(2)	0.4369 (8)	0.1616 (6)	0.1963 (4)	6.0
P1R2H(3)	-0.3519 (6)	0.0132 (7)	0.4358 (6)	6.0	P2R2H(3)	0.5556 (10)	0.2040 (7)	0.2884 (7)	6.0
P1R2H(4)	-0.2341 (9)	-0.0326 (7)	0.5257 (4)	6.0	P2R2H(4)	0.5489 (10)	0.1566 (9)	0.4049 (5)	6.0
P1R2H(5)	-0.0601 (8)	-0.0652 (5)	0.4980 (4)	6.0	P2R2H(5)	0.4243 (9)	0.0672 (6)	0.4299 (4)	6.0
P1R2H(6)	-0.0034 (5)	-0.0519 (6)	0.3795 (6)	6.0	P2R2H(6)	0.3057 (10)	0.0248 (7)	0.3378 (6)	6.0
P1R3C(1)	-0.1852 (8)	0.0489 (5)	0.1919 (4)	3.0 (3)	P2R3C(1)	0.2570 (10)	0.1241 (4)	0.1199 (4)	3.3 (3)
P1R3C(2)	-0.2731 (7)	0.0790 (4)	0.0776 (3)	6.5 (5)	P2R3C(2)	0.2520 (9)	0.1060 (3)	0.0470 (4)	5.2 (4)
P1R3C(3)	-0.3039 (9)	0.1450 (5)	0.1056 (4)	5.9 (5)	P2R3C(3)	0.2358 (6)	0.1594 (5)	-0.0050 (3)	6.4 (4)
P1R3C(4)	-0.2754 (13)	0.1629 (4)	0.1767 (5)	5.5 (4)	P2R3C(4)	0.2245 (10)	0.2309 (4)	0.0159 (4)	6.2 (4)
P1R3C(5)	-0.2161 (7)	0.1149 (4)	0.2198 (3)	5.3 (4)	P2R3C(5)	0.2296 (9)	0.2490 (3)	0.0888 (5)	5.7 (4)
P1R3C(6)	-0.2137 (12)	0.0309 (4)	0.1208 (4)	4.5 (3)	P2R3C(6)	0.2458 (5)	0.1956 (4)	0.1408 (3)	4.6 (4)
P1R3H(2)	-0.2924 (11)	0.0665 (6)	0.0291 (3)	6.0	P2R3H(2)	0.2597 (14)	0.0572 (4)	0.0330 (6)	6.0
P1R3H(3)	-0.3445 (14)	0.1779 (7)	0.0764 (6)	6.0	P2R3H(3)	0.2323 (8)	0.1473 (6)	-0.0548 (3)	6.0
P1R3H(4)	-0.2965 (20)	0.2080 (6)	0.1958 (6)	6.0	P2R3H(4)	0.2135 (16)	0.2674 (5)	-0.0196 (5)	6.0
P1R3H(5)	-0.1968 (11)	0.1273 (5)	0.2683 (4)	6.0	P2R3H(5)	0.2219 (14)	0.2978 (3)	0.1028 (6)	6.0
P1R3H(6)	-0.1927 (20)	-0.0141 (6)	0.1017 (5)	6.0	P2R3H(6)	0.2493 (7)	0.2077 (6)	0.1906 (3)	6.0

^a See Table I for overall group temperature factors. Individual hydrogen atom temperature factors were not refined.

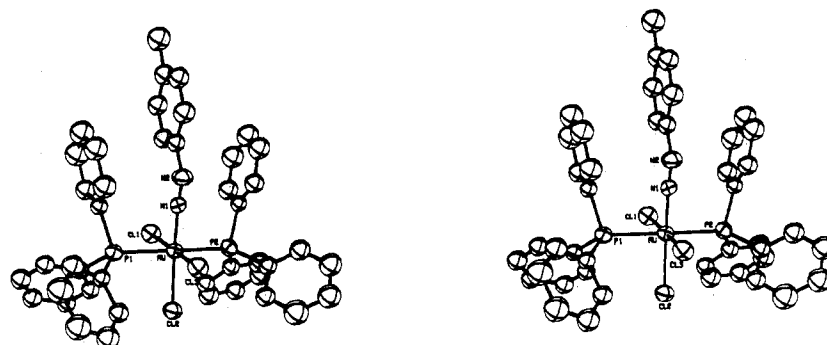


Figure 1. A stereoscopic view of the complex $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$.

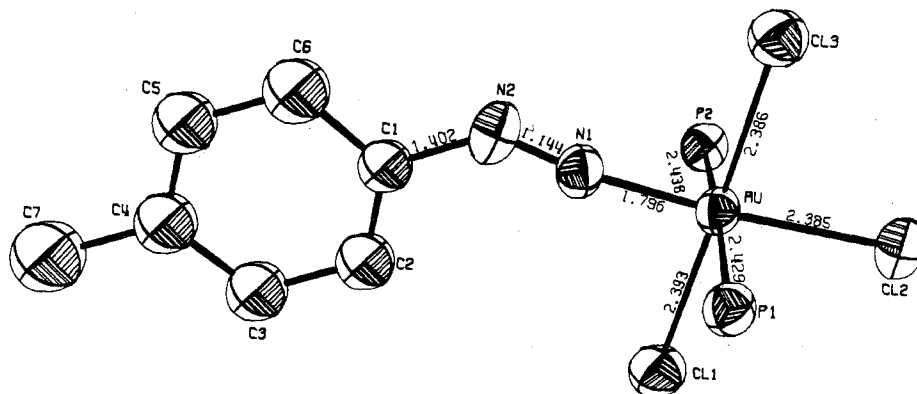


Figure 2. A perspective view of the coordination geometry of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ showing the labeling scheme employed for the non-group atoms. The phenyl rings of the phosphines are omitted.

mated. On the final difference Fourier map, the highest peak was in the region of the acetone molecule with a value of $0.92 \text{ e}/\text{\AA}^3$, or approximately 50% of the height of a ring carbon atom in this struc-

ture. In order to provide a final check on the importance of the acetone molecule in our calculated model, a structure factor calculation omitting the solvent molecule was performed, yielding signif-

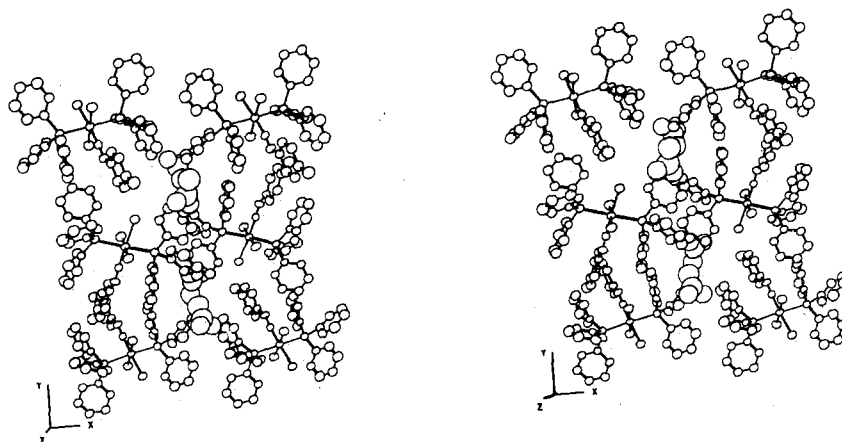


Figure 3. A stereoscopic view of the crystal packing of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2 \cdot \text{Me}_2\text{CO}$.

icantly larger discrepancy factors R and R' of 0.059 and 0.107, respectively. Inclusion of the disordered solvent molecule was thus justified.

The parameters obtained from the final cycle of refinement are taken as the final parameters for the structure and are presented in Table I along with their estimated standard deviations as obtained from the inverse matrix. Table II lists the fractional coordinates of the ring carbon atoms and their individual isotropic temperature factors. In Table III, the root-mean-square amplitudes of vibration for the anisotropically refined atoms are given. A table of the F_o and $|F_c|$ values for the 2478 reflections included in the refinement is available.⁴²

Description of the Structure and Discussion

The molecular structure of $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ is best described as having an octahedral coordination geometry with the triphenylphosphine ligands occupying trans positions as shown in Figure 1. All important intramolecular distances and angles are tabulated in Table IV, and selected least-squares planes with deviations of the atoms from these planes are given in Table V. Figure 2 presents a view of the complex in which the phenyl rings of the phosphine ligands have been omitted for clarity.

The most interesting feature of the structure concerns the coordination of the *p*-tolylazo group. We find an essentially linear mode of coordination for this group with a Ru-N distance of 1.796 (9) Å and a Ru-N-N bond angle of 171.2 (9)°. The Ru-N distance is only slightly (and possibly not significantly) longer than the corresponding values found in ruthenium complexes having linearly coordinated nitrosyls^{20-23,25} and is significantly shorter than the Ru-N(amine) distances reported for a number of ruthenium(II)-amine complexes.^{43,44} This value then is taken as indicative of a strong π interaction between the metal d_{π} orbitals and the p orbitals of the essentially sp hybridized donor atom N(1). The N(1)-N(2) bond length of 1.144 (10) Å is intermediate between a nitrogen-nitrogen double and triple bond, and the N(1)-N(2)-C(1) bond angle of 135.9 (11)° indicates that N(2), unlike N(1), possesses a hybridization more nearly trigonal than linear. This arrangement of the *p*-tolylazo group is similar to that reported by Duckworth, *et al.*,³⁰ for the phenylazo

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Ru	0.174 (3)	0.189 (2)	0.209 (2)
Cl(1)	0.204 (5)	0.233 (5)	0.264 (4)
Cl(2)	0.202 (5)	0.239 (5)	0.263 (5)
Cl(3)	0.210 (5)	0.227 (5)	0.261 (4)
P(1)	0.189 (5)	0.196 (7)	0.214 (6)
P(2)	0.185 (5)	0.214 (5)	0.221 (6)
N(1)	0.185 (17)	0.196 (15)	0.240 (14)
N(2)	0.186 (17)	0.250 (15)	0.261 (15)

Table IV. Principal Intramolecular Distances and Angles for $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2 \cdot \text{Me}_2\text{CO}$

Atoms	Dist, Å	Atoms	Angle, deg
Ru-Cl(1)	2.393 (3)	Ru-N(1)-N(2)	171.2 (9)
Ru-Cl(2)	2.385 (3)	N(1)-N(2)-C(1)	135.9 (11)
Ru-Cl(3)	2.386 (3)	N(1)-Ru-Cl(2)	175.5 (3)
Ru-P(1)	2.429 (4)	Cl(1)-Ru-Cl(3)	177.1 (1)
Ru-P(2)	2.438 (4)	P(1)-Ru-P(2)	173.5 (1)
Ru-N(1)	1.796 (9)	N(1)-Ru-Cl(1)	89.7 (3)
N(1)-N(2)	1.144 (10)	N(1)-Ru-Cl(3)	88.3 (3)
N(2)-C(1)	1.40 (1)	N(1)-Ru-P(1)	90.7 (3)
C(1)-C(2)	1.36 (2)	N(1)-Ru-P(2)	90.1 (3)
C(1)-C(6)	1.41 (2)	Cl(1)-Ru-Cl(2)	94.6 (1)
C(2)-C(3)	1.42 (2)	Cl(1)-Ru-P(1)	87.3 (1)
C(3)-C(4)	1.41 (1)	Cl(1)-Ru-P(2)	86.3 (1)
C(4)-C(5)	1.37 (2)	Cl(2)-Ru-Cl(3)	87.5 (1)
C(4)-C(7)	1.54 (2)	Cl(2)-Ru-P(1)	90.8 (1)
C(5)-C(6)	1.41 (2)	Cl(2)-Ru-P(2)	89.0 (1)
C(2)-H(2)	0.69 (13)	Cl(3)-Ru-P(1)	90.6 (1)
C(3)-H(3)	1.12 (13)	Cl(3)-Ru-P(2)	95.8 (1)
C(5)-H(5)	0.98 (13)	N(2)-C(1)-C(2)	121 (1)
C(6)-H(6)	1.03 (13)	N(2)-C(1)-C(6)	117 (1)
P(1)-P1R1C(1)	1.840 (7)	C(1)-C(2)-C(3)	120 (1)
P(1)-P1R2C(1)	1.836 (7)	C(2)-C(3)-C(4)	120 (1)
P(1)-P1R3C(1)	1.819 (10)	C(3)-C(4)-C(5)	119 (1)
P(2)-P2R1C(1)	1.847 (8)	C(4)-C(5)-C(6)	122 (1)
P(2)-P2R2C(1)	1.836 (10)	C(5)-C(6)-C(1)	118 (1)
P(2)-P2R3C(1)	1.826 (8)	C(6)-C(1)-C(2)	122 (1)
Ac(1)-Ac(2)	1.33 (4)	C(3)-C(4)-C(7)	119 (1)
Ac(1)-Ac(3)	1.36 (4)	C(5)-C(4)-C(7)	122 (1)
Ac(1)-Ac(4)	1.29 (4)	Ac(2)-Ac(1)-Ac(3)	124 (4)
		Ac(2)-Ac(1)-Ac(4)	96 (4)
		Ac(3)-Ac(1)-Ac(4)	140 (4)

complex $\text{ReCl}_2(\text{N}_2\text{C}_6\text{H}_5)(\text{PMe}_2\text{Ph})_3$ and by Avitabile, *et al.*,³¹ for the complex $(\text{HB}(\text{pz})_3)_2\text{Mo}(\text{CO})_2(\text{N}_2\text{C}_6\text{H}_5)(\text{HB}(\text{pz})_3 = \text{hydrotris}(1\text{-pyrazolyl})\text{borate})$. In those cases, the N-N bond length and the M-N-N and N-N-C bond angles for each structure are 1.23 Å, 172°, and 118° and 1.211 (6) Å, 174.2 (1)°, and 121.1 (2)°, respectively. In contrast with this arrangement for the arylazo group, Einstein, *et al.*,³³ observed that the reaction of a diazonium cation with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ yields a system in which the Ir-N-N unit is required to be bent by virtue of chelate ring formation. The iridium-

(42) The table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1676.

(43) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

(44) I. M. Trietel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 6512 (1969).

Table V. Weighted Least-Squares Planes (in Monoclinic Coordinates) and the Distances of Atoms from Their Respective Planes^a

Atom	Dist, Å	Atom	Dist, Å
Plane through Ru, Cl(1), Cl(3), P(1), P(2) $-3.96x + 15.91y - 7.28z = -1.55$			
Ru	-0.003 (1)	P(1)	-0.017 (3)
Cl(1)	0.042 (3)	P(2)	-0.017 (3)
Cl(3)	0.039 (3)		
Plane through Ru, Cl(2), P(1), P(2), N(1) $0.75x + 9.37y + 15.91z = 3.83$			
Ru	0.019 (1)	P(2)	-0.123 (3)
Cl(2)	0.017 (3)	N(1)	0.156 (9)
P(1)	-0.112 (3)		
Plane through Ru and Arylazo Ligand $11.82x + 4.90y - 4.33z = 0.16$			
Ru	-0.001 (1)	C(3)	0.02 (1)
N(1)	0.018 (9)	C(4)	-0.03 (1)
N(2)	0.031 (10)	C(5)	-0.02 (1)
C(1)	0.01 (1)	C(6)	-0.03 (1)
C(2)	0.05 (1)	C(7)	-0.02 (1)

^a Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961).

nitrogen distance in this case is considerably longer than Ir-N distances found in linearly coordinated nitrosyl complexes^{15,19} and is more nearly consistent with corresponding values for complexes having bent NO groups.^{11,12,17,18} In addition, the donor nitrogen atom is protonated in $[\text{IrCl}(\text{NHNC}_6\text{H}_3\text{F})(\text{CO})(\text{PPh}_3)_2]^+$ as reported by Einstein, *et al.*³³

The present structural results when coupled with the simple bonding picture conveyed by structures I and II lead us to describe the coordination of the arylazo group in $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$ in terms of resonance forms Ia and Ib with the latter clearly dominant as indicated by the bond angle at N(2). We thus consider the arylazo group to coordinate as formally ArN_2^+ (or as a three-electron donor) if the M-N-N group is linear or approximately so. In the case of the title complex, this formalism dictates a Ru(II) metal ion which is consistent with the observed octahedral geometry and related structural parameters and with the formulation of the isoelectronic complex $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$ as Ru(II)-

NO^+ . This formalism is different from that proposed by Duckworth, *et al.*,³⁰ in which the linearly coordinated arylazo group was considered as ArN_2^- . We believe our proposal as a formalism is more reasonable based on the simple bonding notions and the analogy to nitrosyl systems. A more detailed view of the bonding involves σ -bond formation using a nitrogen sp hybrid and π -back-bonding in which the arylazo acceptor functions are the nondegenerate $\pi^*(\text{NN})$ orbital and the remaining N(1) p orbital in the plane defined by N(1), N(2), and C(1). Clearly, the degeneracy of the π -back-bonding interaction found in NO^+ complexes of trigonal or higher symmetry is removed in the present case.

Other parameters in the structure are more or less as expected. The average Ru-P and Ru-Cl distances of 2.434 (4) and 2.388 (3) Å compare favorably with corresponding values of 2.426 (6) and 2.362 (6) Å found in $\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2^+$ ²¹ and with 2.39 (2) and 2.388 (6) Å found in $\text{RuCl}_2(\text{PPh}_3)_3$.⁴⁵ Moreover, angular distortions from ideal octahedral coordination are rather slight with the three trans angles ranging from 173.5 (1) to 177.1 (1)°. The intermolecular contacts in the structure are normal and are therefore not tabulated. In Figure 3, a stereoscopic view of the packing of the complex is presented.⁴⁶

Registry No. $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2 \cdot \text{CH}_3\text{COOCH}_3$, 39834-85-0.

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(45) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(46) Note Added in Proof. While this paper was in press, it became known to us that the structure of this same complex was also determined by B. L. Haymore and J. A. Ibers of Northwestern University. Their results agree completely with ours. All distances are within one estimated standard deviation of the results reported above except for Ru-N which is within 2 esd's and N-C which is within 3 esd's. Haymore and Ibers' values for the coordinated p-tolylazo group are: Ru-N, 1.779 Å; N-N, 1.158 Å; N-C, 1.368 Å; Ru-N-N, 172°; N-N-C, 137°.