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## Aryldiazo Complexes. Structure of a Hydrido-Aryldiazo Complex of Osmium, OsH(CO)(N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>

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Received June 3, 1975

AIC50374V

The structure of OsH(CO)(N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> has been determined crystallographically and consists of discrete molecules of the aryldiazo complex and solvent. This complex of Os(0) is five-coordinate and has a distorted trigonal-bipyramidal coordination geometry about the osmium atom. Owing to the reduced steric requirements of the hydrido ligand, the P(1)-Os-P(2) and N(1)-Os-C(1) angles change from the respective idealized values of 180 and 120° to 164.37 (6) and 138.0 (3)° indicating a distortion toward a quasitetrahedral geometry. The singly bent, phenyldiazo ligand occupies an equatorial coordination site and possesses an unusually long osmium-nitrogen bond length with Os-N = 1.867 (6) Å, N-N = 1.211 (8) Å, N-C = 1.460 (10) Å, Os-N-N = 171.1 (6)°, and N-N-C = 118.5 (7)°. The compound crystallizes from dichloromethane as solvated crystals in space group *Ci*<sup>1</sup>-*P1* of the triclinic system with *a* = 13.440 (2) Å, *b* = 13.481 (1) Å, *c* = 12.528 (2) Å, *α* = 114.30 (1)°, *β* = 101.82 (1)°, *γ* = 81.43 (1)°, and *Z* = 2. Based upon 5340 unique reflections with *F*<sub>o</sub><sup>2</sup> > 3σ(*F*<sub>o</sub><sup>2</sup>) the structural data were refined by full-matrix, least-squares methods to *R* = 0.046 and *R*<sub>w</sub> = 0.057.

### Introduction

Much current interest has been stimulated in aryldiazo ligands, not only because of their close relationship to nitrosyl and dinitrogen ligands but also because of their varied modes of bonding and their utility as intermediates in the syntheses of aryldiazene and arylhydrazine ligands.<sup>1-9</sup> Structural studies have shown that the aryldiazo ligand can adopt a doubly bent geometry<sup>10,11</sup> or a singly bent geometry<sup>12</sup> or that it can bridge two metal atoms.<sup>13</sup> In this regard, it is similar to the iso-electronic nitrosyl ligand; indeed, nitrosyl and aryldiazo ligands have been compared structurally in almost identical coordination environments, in [RhCl(L)(PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>)] [PF<sub>6</sub>]<sup>10,14,15</sup> (bent Rh-N-N) and in RuCl<sub>3</sub>(L)(PPh<sub>3</sub>)<sub>2</sub><sup>16,17</sup> (linear Ru-N-N) where L = NNAr, NO. The geometry and chemical reactivity seem to be very sensitive to the electronic characteristics of the central metal and especially to the coordination geometry about it. For this reason, structural studies are especially useful in understanding the types of reactions which aryldiazo ligands undergo.

Recently, acyl-, aroyl-, and alkylidiazole ligands have been prepared starting with dinitrogen complexes of rhenium, molybdenum, and tungsten.<sup>18</sup> Many aryldiazo ligands, es-

pecially those attached to Ru, Os, Rh, Ir, and Pt, react with coordinating and noncoordinating protonic acids to form complexes of *cis*-aryldiazene.<sup>2-4,19</sup> A rhenium complex containing a singly bent aryldiazo ligand has been observed to react with H<sup>+</sup> at the nitrogen atom which is attached to the aryl group, thus forming an unsymmetrical form of phenyldiazene, Re=N=NHPh.<sup>20</sup> In an aryldiazo complex the value of ν(NN), when not vibrationally coupled with other ligand modes, is indicative of the mode of coordination of the aryldiazo group.<sup>10,16</sup> Despite the relatively low value of ν(NN) at 1543 cm<sup>-1</sup> for OsH(CO)(NNPh)(PPh<sub>3</sub>)<sub>2</sub>, we felt that it was indicative of a singly bent mode of coordination for the diazo ligand.<sup>21</sup>

For this reason and because this reactive complex is the first hydrido-aryldiazo complex to be synthesized we have determined its solid-state structure crystallographically and report it here. This is the third five-coordinate, aryldiazo complex to be studied crystallographically and the second one found to possess a trigonal-bipyramidal coordination geometry about the metal.<sup>22</sup>

### Experimental Section

**Crystal Preparation.** The title complex was prepared according

Table I. Summary of Crystal Data and Intensity Collection

Compd	$\text{OsH}(\text{CO})(\text{N}_2\text{C}_6\text{H}_5)_2(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{CH}_2\text{Cl}_2$
Formula wt	933.86 amu
Formula	$\text{C}_{44}\text{H}_{38}\text{Cl}_2\text{N}_2\text{OOSp}_2$
<i>a</i>	13.440 (2) Å
<i>b</i>	13.481 (1) Å
<i>c</i>	12.528 (2) Å
$\alpha$	114.30 (1)°
$\beta$	101.82 (1)°
$\gamma$	81.43 (1)°
<i>V</i>	2020 Å <sup>3</sup>
<i>Z</i>	2
Density	1.535 g/cm <sup>3</sup> (calcd) 1.50 (1) g/cm <sup>3</sup> (exptl)
Space group	$C_2^1-P\bar{1}$ (triclinic)
Crystal dimensions	0.28 × 0.20 × 0.09 mm
Crystal shape	Triclinic prism with {011}, {101}, and {211} faces well developed
Crystal vol	0.0043 mm <sup>3</sup>
Temp	22°
Radiation	Cu $K\alpha_1$ ( $\lambda$ 1.54056 Å) prefiltered with 1 mil of Ni foil
Transmission factors	0.259–0.577
$\mu$	82.38 cm <sup>-1</sup>
Receiving aperture	4.0 mm wide by 3.9 mm high; 30 cm from crystal
Takeoff angle	2.8°
Scan speed	2.0° in $2\theta$ /min
Scan range	0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$
Background counts	10 sec
$2\theta$ limits	3.0–126.0°
Final no. of variables	217
Unique data used, $F_o^2 > 3\sigma(F_o^2)$	5340
Error in observation of unit wt	1.75 electrons

to the published method by deprotonating  $\text{OsH}(\text{CO})(\text{HNNPh})_3(\text{PPh}_3)_3^+$  with NaOH in acetone-methanol at  $-20^\circ$ .<sup>23</sup> The resulting brown, microcrystalline powder was recrystallized from dichloromethane in the dark at  $-10^\circ$  to yield beautiful brown crystals of the 1:1 methylene chloride solvate. Because the crystals slowly lost solvent of crystallization, freshly prepared crystals were mounted in capillaries in an atmosphere of the solvent in order to prevent desolvation during data collection. Except for this desolvation, the compound was stable in air under ambient conditions. *Anal.* Calcd for  $\text{C}_{44}\text{H}_{38}\text{Cl}_2\text{N}_2\text{OOSp}_2$ : C, 56.59; H, 4.10; N, 3.00; Cl, 7.59. Found: C, 56.80; H, 4.16; N, 2.76; Cl, 6.86. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. As judged by a color change, brown to black, the powder was slightly photosensitive; however, the larger single crystals seemed to be much less sensitive.

**Crystallographic Data.** Preliminary film data showed the crystals to belong to the triclinic system with extinctions (*hkl*, *h* + *k* + *l* odd) characteristic of the space groups  $C_2^1-P1$  and  $C_2^1-P\bar{1}$ , which are nonstandard settings of  $P1$  and  $P\bar{1}$ . A cell reduction failed to reveal a cell of higher symmetry. The centrosymmetric space group was shown to be the correct one on the basis of the following results: (1) the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices; (2) the clear and distinct location of all 35 phenyl hydrogen atoms in difference Fourier syntheses; (3) the statistical equivalence of the intensities of 152 pairs of reflections related by a center of inversion. For the sake of convenience, intensity data were collected using the body-centered cell and then transformed to the primitive cell prior to the handling and processing of the data.<sup>24</sup> Using a least-squares procedure based on the angular positions of 17 hand-centered reflections in diverse regions of reciprocal space ( $47.6 \leq 2\theta \leq 58.0$ ), accurate unit cell dimensions were determined using a narrow X-ray source. See Table I for pertinent crystal information and details of data collection. The mosaicity of the crystal was found to be acceptable for the  $\theta$ - $2\theta$  scan technique based on  $\omega$  scans performed with an open counter.

Data collection was carried out using a Picker four-circle diffractometer equipped with a scintillation counter and a pulse height analyzer which was adjusted to accept 90% of the Cu  $K\alpha$  peak. Background counts were measured at both ends of the scan range with both the counter and crystal stationary. The intensities of six standard reflections were measured every 100 reflections. These were

found to decrease nearly linearly by about 10% during the course of data collection, presumably as a result of crystal decomposition or desolvation. The observed intensities were modified to correct for this apparent crystal decomposition. The slightly low values of the density for several crystals in the range 1.49–1.51 g/cm<sup>3</sup> indicated that these crystals may have lost some of the solvent of crystallization. The calculated densities with no solvent and with one solvent molecule per osmium atom are 1.395 and 1.535 g/cm<sup>3</sup>, respectively.

The intensities of 6731 reflections were measured ( $h \geq 0$ ) out to  $2\theta = 126^\circ$  using nickel-filtered copper X-radiation; past this point very few reflections were above background. The data were processed in the usual way using a value of 0.04 for  $p$ .<sup>25</sup> Only those 5340 unique reflections with  $F_o^2 > 3\sigma(F_o^2)$  were used in subsequent calculations. An absorption correction was applied to the data using gaussian integration.<sup>26</sup> The *R* index for averaging 152 pairs of symmetry-related reflections was 1.3% after the absorption correction was applied.

**Structure Refinement.** The structure was solved using a sharpened, origin-removed Patterson synthesis to locate the osmium atom and the two trans phosphorus atoms. Subsequent refinements and difference Fourier syntheses using the centrosymmetric space group  $P\bar{1}$  were used to locate the remaining nonhydrogen atoms as well as the 35 phenyl hydrogen atoms. The structure was refined using full-matrix, least-squares techniques. The isotropic model (seven rigid-body phenyl groups and no hydrogen atoms) almost converged to *R* indices of  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.064$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.091$ . During the refinements the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and where the weights, *w*, are taken as  $4F_o^2/\sigma^2(F_o^2)$ . Atomic scattering factors were taken from Cromer and Waber's tabulation.<sup>27</sup> The anomalous dispersion terms for Os, Cl, and P were included in  $F_c$ .<sup>28</sup> All phosphine phenyl groups and also the diazo phenyl group during the first calculations were refined as rigid, planar bodies with a constant and uniform C–C distance of 1.392 Å and with individual isotropic thermal parameters for each carbon atom. Although all phenyl hydrogen atoms were located in the difference Fourier syntheses, their positions were idealized, and they were included as fixed contributions in final anisotropic refinements; the C–H distance was assumed to be 0.98 Å, the CCH angle was assumed to be 120°, and the isotropic thermal parameter of a hydrogen atom was assumed to be 1.0 Å<sup>2</sup> larger than the thermal parameter of the carbon atom to which it was attached. The hydrogen atoms of the solvents, H(1) and H(2), were also placed in idealized positions in a plane normal to the Cl(1)–C(2)–Cl(2) plane (C–H = 1.00 Å, H–C–H = 109°) and were included as fixed contributions. Additional refinements in which the nongroup atoms were treated anisotropically and the hydrogen atom contributions were included converged to give agreement indices of  $R = 0.049$  and  $R_w = 0.062$ . Because five of the six carbon atoms in the diazo phenyl ring had large thermal parameters (in the range 9–13 Å<sup>2</sup>), the six carbon atoms were refined as individual atoms with anisotropic thermal parameters in the last cycles of refinement. The final agreement indices are  $R = 0.046$  and  $R_w = 0.057$  after convergence.

A final difference Fourier synthesis of residual electron density revealed nothing interesting except one peak (2.1 e/Å<sup>3</sup>) located exactly in the trigonal plane near the expected position of the hydrido ligand. The remaining residuals were near the phosphine phenyl groups (0.9–0.6 e/Å<sup>3</sup>) or the solvent (0.9–0.6 e/Å<sup>3</sup>). A typical carbon atom had a height of 4.2 e/Å<sup>3</sup>. Another difference synthesis using only data with  $(\sin \theta)/\lambda \leq 0.35 \text{ \AA}^{-1}$  caused the large peak in the trigonal plane to decrease in height (1.0 e/Å<sup>3</sup>) but its position did not change significantly. This electron density seems to come primarily from the hydrido ligand, but its position, 1.2 Å from Os (expected Os–H  $\approx 1.7 \text{ \AA}$ ),<sup>29</sup> and its height are apparently altered by the presence of osmium residuals. A comparison of the observed and calculated structure amplitudes showed no need for an extinction correction. In order to check for the possibility of desolvation of the data crystal, the occupancy factor for the entire solvent molecule was refined during most of the least-squares refinements. Because the value of this factor remained near unity (0.934 (6)), the value of the occupancy factor was set at 1.0 and not refined during the last several cycles of anisotropic refinement. All but two unobserved reflections obey the relation  $|F_c^2 - F_o^2| < 4\sigma(F_o^2)$ . There were no trends of the quantity  $\sum w(|F_o| - |F_c|)^2$  as a function of  $|F_o|$ , diffractometer setting angles, or Miller indices.

The final positional and thermal parameters of atoms and groups appear in Tables II–IV, and root-mean-square amplitudes of vibration

Table II. Positional and Thermal Parameters for the Nongroup Atoms of  $\text{OsH}(\text{CO})(\text{N}_2\text{Ph})(\text{PPh}_3)_2$ 

ATOM	X <sup>A</sup>	Y	Z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
OS	0.153620(26)	0.207486(26)	0.28688(3)	5.72(2)	5.74(3)	7.98(3)	-0.35(2)	0.61(2)	2.72(2)
P(1)	0.28849(15)	0.11872(15)	0.37122(16)	5.90(12)	6.74(14)	7.22(16)	-0.20(10)	1.04(11)	2.81(12)
P(2)	0.03640(15)	0.26652(15)	0.15512(17)	5.84(12)	5.69(13)	6.07(17)	-0.18(10)	1.08(11)	2.53(12)
CL(1)	0.3204(4)	0.5143(3)	0.0908(6)	22.8(5)	15.1(3)	52.1(11)	-2.7(3)	6.4(6)	4.8(5)
CL(2)	0.4716(4)	0.3448(5)	0.0656(5)	19.2(5)	33.0(7)	31.9(8)	-0.3(5)	1.6(5)	14.7(6)
C(2)	0.4112(12)	0.4338(12)	0.1623(12)	20.7(15)	18.9(14)	18.4(16)	-8.6(12)	3.8(12)	7.1(13)
N(1)	0.2332(5)	0.3240(5)	0.3281(6)	6.2(4)	6.6(5)	9.7(6)	-0.4(4)	0.5(4)	3.3(4)
N(2)	0.2928(5)	0.3896(5)	0.3438(6)	8.1(5)	7.7(5)	10.1(7)	-0.9(4)	1.4(5)	2.8(5)
C(1)	0.0575(6)	0.1695(6)	0.3506(7)	7.9(6)	7.0(6)	7.9(7)	-0.6(5)	0.2(5)	2.8(5)
O(1)	0.0000(5)	0.1514(5)	0.3966(6)	10.9(6)	12.3(6)	14.6(7)	-2.1(5)	4.8(5)	5.1(6)
C11	0.2971(7)	0.4892(7)	0.4517(8)	8.4(7)	7.5(6)	10.6(8)	-1.2(5)	2.1(6)	2.7(6)
C12	0.2338(10)	0.5169(10)	0.5292(10)	17.9(13)	15.9(12)	18.0(13)	-7.5(10)	9.3(11)	-4.8(10)
C13	0.2476(12)	0.6146(13)	0.6321(11)	22.1(18)	23.4(17)	18.9(14)	-9.5(14)	13.0(14)	-7.0(13)
C14	0.3199(13)	0.6778(10)	0.6532(11)	20.2(16)	10.6(10)	13.5(13)	-3.7(10)	5.0(12)	-0.6(9)
C15	0.3824(11)	0.6504(9)	0.5769(11)	20.3(14)	11.7(10)	14.5(14)	-9.0(10)	1.9(11)	1.5(10)
C16	0.3720(13)	0.5551(10)	0.4736(9)	17.5(12)	14.7(11)	12.9(11)	-8.1(10)	4.5(9)	1.5(9)

<sup>A</sup> ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. <sup>B</sup> THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS  $\text{EXP}[-(B_{11}H^2 + B_{22}K^2 + B_{33}L^2 + 2B_{12}HK + 2B_{13}HL + 2B_{23}KL)]$ . THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS  $\times 10^{-3}$ .

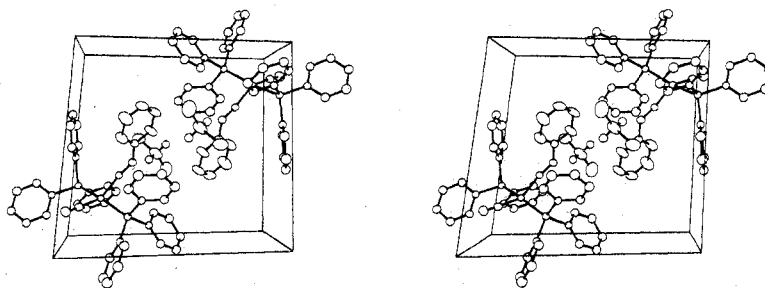


Figure 1. Stereoview of a unit cell of  $\text{OsH}(\text{CO})(\text{NNPh})(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$ . The  $x$  axis is horizontal to the right, the  $y$  axis is almost vertical, and the  $z$  axis is perpendicular to the paper coming toward the reader. The vibrational ellipsoids are drawn at the 20% probability level. The phenyl hydrogen atoms have been omitted.

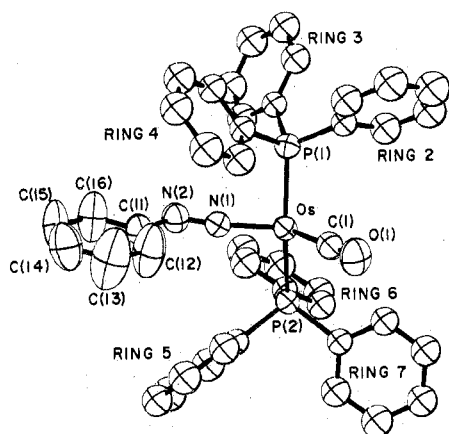


Figure 2. Perspective view of  $\text{OsH}(\text{CO})(\text{NNPh})(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$  showing the lettering and numbering scheme. The solvent molecule and phenyl hydrogen atoms have been omitted. The vibrational ellipsoids are drawn at the 50% probability level.

are given in Table V. A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.<sup>30</sup>

## Discussion

**Description of the Structure.** The structure of  $\text{OsH}(\text{CO})(\text{NNPh})(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$  consists of molecules of the osmium complex and of the solvent with two molecules of the complex and two solvent molecules in the unit cell as shown in the stereodrawing of the unit cell, Figure 1. A perspective view of the complex together with the numbering scheme is shown in Figure 2. The complex has a trigonal-bipyramidal coordination geometry, but it is somewhat distorted owing to the reduced steric requirements of the hydrido ligand. Similar distortions have been observed in  $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$ ,<sup>31</sup>

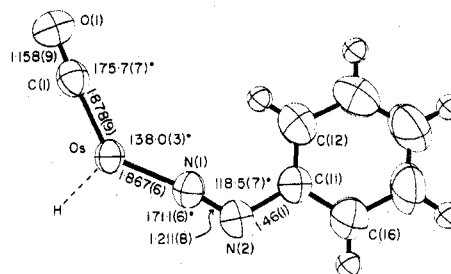


Figure 3. Trigonal coordination plane with some bond angles and distances for  $\text{OsH}(\text{CO})(\text{NNPh})(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$ . The approximate location of the hydrido ligand is shown. The vibrational ellipsoids are drawn at the 50% probability level.

$\text{RuHCl}(\text{PPh}_3)_3$ ,<sup>32</sup>  $\text{CoH}(\text{PF}_3)_4$ ,<sup>33</sup> and  $\text{RhH}(\text{PPh}_3)_4$ .<sup>34</sup> The phosphine ligands occupy the two axial sites and are approximately trans to each other. However, they both bend directly toward the hydrido ligand by somewhat differing amounts,  $4.0(4)^\circ$  for P(1) and  $11.6(5)^\circ$  for P(2), causing the P(1)-Os-P(2) angle to decrease to  $164.37(6)^\circ$  (see Table VI). This can be compared with the same angle in  $[\text{Fe}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2][\text{BF}_4]$ <sup>22</sup> at  $175.85(8)^\circ$  and in  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ <sup>35</sup> at  $180^\circ$  (symmetry imposed).

The phenyldiazo, carbonyl, and hydrido ligands all lie in the trigonal plane. Figure 3 shows the trigonal coordination plane together with some pertinent bond distances and angles. The phenyldiazo and carbonyl ligands both move toward the hydrido ligand and away from each other, thus causing the C(1)-Os-N(1) angle to open up to  $138.0(3)^\circ$ ; compare this to the same angle in the cationic dicarbonyl complex of iron at  $121.4(3)^\circ$ . The carbonyl ligand is essentially linear, but it is bent by a small, significant amount,  $4.3(7)^\circ$ . The oxygen atom of the carbonyl ligand remains almost exactly in the

Table III

DERIVED PARAMETERS FOR THE RIGID GROUP ATOMS OF  
OS<sub>2</sub>(CO)<sub>2</sub>(N<sub>2</sub>PH)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

ATOM	X	Y	Z	B <sub>r</sub> A <sup>2</sup>	ATOM	X	Y	Z	B <sub>r</sub> A <sup>2</sup>
C21	0.2607(4)	-0.0008(4)	0.3898(5)	4.29(14)	C51	0.0139(4)	0.4151(3)	0.2083(5)	4.14(14)
C22	0.2811(5)	-0.0089(4)	0.4995(4)	6.31(21)	C52	0.0164(5)	0.4741(5)	0.1402(4)	6.64(22)
C23	0.2589(5)	-0.1022(6)	0.5091(5)	7.45(25)	C53	0.0016(5)	0.5874(5)	0.1889(5)	7.48(25)
C24	0.2163(5)	-0.1874(4)	0.4090(6)	7.76(26)	C54	-0.0155(5)	0.6418(3)	0.3056(5)	5.98(19)
C25	0.1959(5)	-0.1793(4)	0.2993(5)	6.94(23)	C55	-0.0180(5)	0.5829(4)	0.3737(4)	6.77(21)
C26	0.2181(5)	-0.0860(5)	0.2897(4)	6.03(20)	C56	-0.0033(5)	0.4696(4)	0.3250(4)	5.94(19)
C31	0.3943(3)	0.0679(4)	0.2864(4)	3.97(13)	C61	0.0843(4)	0.2242(4)	0.0149(4)	4.15(14)
C32	0.4542(4)	-0.0261(4)	0.2849(5)	5.44(18)	C62	0.0308(3)	0.1579(4)	-0.0927(5)	5.04(16)
C33	0.5358(4)	-0.0622(4)	0.2222(5)	5.96(19)	C63	0.0723(4)	0.1233(4)	-0.1965(4)	5.89(19)
C34	0.5575(4)	-0.0043(5)	0.1609(5)	6.12(20)	C64	0.1673(4)	0.1551(5)	-0.1926(4)	6.16(20)
C35	0.4977(4)	0.0897(5)	0.1623(5)	6.24(21)	C65	0.2208(3)	0.2215(5)	-0.0850(5)	6.66(21)
C36	0.4161(4)	0.1258(4)	0.2251(5)	5.61(18)	C66	0.1793(4)	0.2560(4)	0.0187(4)	5.89(19)
C41	0.3482(4)	0.2059(4)	0.5186(4)	4.33(14)	C71	-0.0911(3)	0.2187(4)	0.1061(5)	4.13(14)
C42	0.4531(4)	0.2114(4)	0.5534(5)	5.21(17)	C72	-0.1059(3)	0.1168(4)	0.1011(5)	4.96(16)
C43	0.4926(3)	0.2789(5)	0.6684(5)	6.59(21)	C73	-0.2016(4)	0.0756(3)	0.0569(5)	5.68(18)
C44	0.4271(5)	0.3409(5)	0.7487(4)	6.98(22)	C74	-0.2824(3)	0.1362(5)	0.0178(5)	5.97(19)
C45	0.3222(4)	0.3353(5)	0.7140(5)	7.45(24)	C75	-0.2676(4)	0.2381(4)	0.0228(5)	6.42(21)
C46	0.2828(3)	0.2679(5)	0.5990(5)	6.41(21)	C76	-0.1719(4)	0.2794(3)	0.0669(5)	5.56(18)

RIGID GROUP PARAMETERS

GROUP	X <sub>C</sub> <sup>A</sup>	Y <sub>C</sub>	Z <sub>C</sub>	DELTA <sup>B</sup>	EPSILON	ETA
RING2	0.23849(29)	-0.0941(3)	0.3994(4)	1.872(10)	1.923(4)	2.808(10)
RING3	0.47593(28)	0.0318(3)	0.2236(3)	0.216(3)	2.889(3)	-0.721(3)
RING4	0.3877(3)	0.2734(3)	0.6337(3)	1.489(4)	-2.767(3)	1.251(4)
RING5	-0.00082(28)	0.5285(3)	0.2570(3)	-3.382(9)	-2.037(3)	1.216(8)
RING6	0.12579(28)	0.18968(29)	-0.0889(3)	-1.078(4)	-2.733(3)	-1.482(4)
RING7	-0.18676(28)	0.1775(3)	0.0619(3)	0.370(3)	3.037(3)	-2.922(3)

<sup>A</sup>X<sub>C</sub>, Y<sub>C</sub>, AND Z<sub>C</sub> ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. <sup>B</sup>THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETARADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, *ACTA CRYSTALLOGR.*, 18, 511(1965).

Table IV. Idealized Positional Coordinates for Hydrogen Atoms

Atom	x	y	z	Atom	x	y	z
H(12)	0.177	0.472	0.517	H(46)	0.211	0.264	0.576
H(13)	0.194	0.634	0.688	H(52)	0.026	0.437	0.059
H(14)	0.324	0.746	0.723	H(53)	0.002	0.628	0.141
H(15)	0.439	0.697	0.588	H(54)	-0.024	0.720	0.338
H(16)	0.422	0.535	0.418	H(55)	-0.027	0.621	0.454
H(22)	0.311	0.048	0.567	H(56)	-0.003	0.431	0.372
H(23)	0.272	-0.108	0.583	H(62)	-0.034	0.136	-0.096
H(24)	0.200	-0.251	0.415	H(63)	0.036	0.077	-0.270
H(25)	0.166	-0.238	0.230	H(64)	0.196	0.131	-0.264
H(26)	0.204	-0.081	0.214	H(65)	0.285	0.243	-0.083
H(32)	0.439	-0.066	0.326	H(66)	0.216	0.302	0.092
H(33)	0.577	-0.127	0.221	H(72)	-0.051	0.075	0.127
H(34)	0.614	-0.029	0.118	H(73)	-0.213	0.006	0.053
H(35)	0.513	0.130	0.121	H(74)	-0.349	0.108	-0.012
H(36)	0.376	0.190	0.226	H(75)	-0.324	0.280	-0.004
H(42)	0.498	0.169	0.499	H(76)	-0.162	0.349	0.071
H(43)	0.564	0.284	0.692	H(1) <sup>a</sup>	0.460	0.483	0.228
H(44)	0.454	0.390	0.827	H(2) <sup>a</sup>	0.373	0.398	0.195
H(45)	0.278	0.379	0.769				

<sup>a</sup> These hydrogen atoms are attached to the solvent molecule.

trigonal plane and bends toward the aryldiazo ligand which is a good  $\pi$ -acceptor ligand. Although hydrogen atoms are not easy to find, especially when they are near very heavy metal atoms, the presence of the hydrido ligand was verified through several means. (1) The largest peak of residual electron density was found in the trigonal plane very near the location expected for the hydrido ligand (see Experimental Section). (2) The coordination geometry about the osmium atom indicates the presence of a stereochemically active ligand located approximately in the trigonal plane. (3) The proton NMR spectra of dissolved single crystals of this osmium complex show a distinct 1:2:1 triplet at  $\tau$  19.5 with  $J_{PH} = 21$  Hz in  $CD_2Cl_2$ . (4) Infrared spectra of crushed single crystals show the Os-H stretching vibration at  $2010\text{ cm}^{-1}$ ;  $\nu(CO) = 1911\text{ cm}^{-1}$ .

Table V. Root-Mean-Square Amplitudes of Vibration ( $\text{\AA}$ ) for  $OsH(CO)(NPh)(PPh_3)_2 \cdot CH_2Cl_2$ 

Atom	Min	Intermed	Max
Os	0.2073 (5)	0.2182 (5)	0.2361 (4)
P(1)	0.215 (2)	0.222 (2)	0.232 (2)
P(2)	0.207 (2)	0.226 (2)	0.232 (2)
N(1)	0.221 (8)	0.230 (8)	0.258 (8)
N(2)	0.238 (9)	0.265 (8)	0.267 (9)
C(1)	0.221 (10)	0.232 (10)	0.273 (10)
O(1)	0.244 (8)	0.305 (8)	0.345 (9)
C(2)	0.283 (13)	0.348 (15)	0.472 (17)
Cl(1)	0.336 (4)	0.443 (5)	0.624 (7)
Cl(2)	0.396 (5)	0.460 (5)	0.504 (6)
C(11)	0.235 (10)	0.257 (10)	0.282 (11)
C(12)	0.247 (12)	0.306 (14)	0.529 (16)
C(13)	0.240 (11)	0.346 (18)	0.607 (20)
C(14)	0.239 (14)	0.349 (16)	0.433 (16)
C(15)	0.223 (12)	0.329 (15)	0.457 (16)
C(16)	0.259 (13)	0.278 (12)	0.452 (14)

The distances and angles in the osmium complex are in the range to be expected for osmium-carbonyl-phosphine complexes. Although the average Os-P distance of 2.337 (5)  $\text{\AA}$  falls in the expected range of 2.33-2.43  $\text{\AA}$ , it is the shortest distance observed in osmium complexes which have two trans triphenylphosphine ligands. The average Os-P distance in  $[Os(CO)_2(NO)(PPh_3)_2][ClO_4]^{36}$  is 2.406 (4)  $\text{\AA}$ . The Os-C distance at 1.878 (9)  $\text{\AA}$  and the C-O distance at 1.158 (9)  $\text{\AA}$  are typical. Both phosphine ligands adopt the common propeller conformation, and none of the Os-P-C-C torsion angles is unusual. There are no significant intramolecular interactions (<2.5  $\text{\AA}$ ) in the complex. The phosphine ligand associated with P(1) is oriented about the Os-P bond in a staggered fashion with respect to the ligands in the trigonal plane, but the other phosphine ligand is approximately oriented in an eclipsed fashion; rings 5, 6, and 7 are oriented near the phenyldiazo, hydrido, and carbonyl ligands, respectively.

Table VI. Selected Distances (Å) and Angles (deg) in OsH(CO)(NNPh)(PPh<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>

Bond Distances			
Os-P(1)	2.333 (2)	Os-P(2)	2.341 (2)
Os-C(1)	1.878 (9)	Os-N(1)	1.867 (6)
C(1)-O(1)	1.158 (9)	N(1)-N(2)	1.211 (8)
N(2)-C(11)	1.460 (10)	C(11)-C(12)	1.323 (13)
C(12)-C(13)	1.417 (15)	C(13)-C(14)	1.302 (17)
C(14)-C(15)	1.304 (16)	C(15)-C(16)	1.399 (14)
C(16)-C(11)	1.353 (12)	C(2)-Cl(1)	1.851 (16)
C(2)-Cl(2)	1.576 (16)	P(1)-C(21)	1.820 (7)
P(1)-C(31)	1.831 (5)	P(1)-C(41)	1.823 (4)
P(2)-C(51)	1.831 (4)	P(2)-C(61)	1.832 (5)
P(2)-C(71)	1.817 (5)		
Nonbonded Distances			
H(1)-N(2)	2.38	C(1)-H(72)	2.74
N(1)-H(12)	2.56	H(12)-H(56)	2.69
N(1)-H(36)	2.58	C(1)-C(21)	3.39
N(2)-H(16)	2.56	N(2)-H(12)	2.69
Bond Angles			
P(1)-Os-P(2)	164.37 (6)	N(1)-Os-C(1)	138.0 (3)
P(1)-Os-C(1)	92.5 (2)	P(1)-Os-N(1)	90.2 (2)
P(2)-Os-C(1)	96.7 (2)	P(2)-Os-N(1)	91.3 (2)
Os-C(1)-O(1)	175.7 (7)	Os-N(1)-N(2)	171.1 (6)
N(1)-N(2)-C(11)	118.5 (7)	C(12)-C(11)-N(2)	123.9 (8)
C(16)-C(11)-N(2)	117.2 (8)	C(12)-C(11)-C(16)	118.9 (9)
C(11)-C(12)-C(13)	118.4 (11)	C(12)-C(13)-C(14)	122.7 (11)
C(13)-C(14)-C(15)	118.9 (11)	C(14)-C(15)-C(16)	120.8 (11)
C(15)-C(16)-C(11)	120.3 (11)	Os-P(1)-C(31)	113.4 (2)
Os-P(1)-C(21)	117.2 (2)	Os-P(2)-C(51)	113.7 (2)
Os-P(1)-C(41)	113.8 (2)	Os-P(2)-C(71)	120.1 (2)
Os-P(2)-C(61)	110.2 (2)	C(21)-P(1)-C(41)	104.1 (3)
C(21)-P(1)-C(31)	103.3 (3)	C(51)-P(2)-C(61)	105.2 (3)
C(31)-P(1)-C(41)	103.6 (2)	C(61)-P(2)-C(71)	102.4 (2)
C(51)-P(2)-C(71)	103.6 (2)	Cl(1)-C(2)-Cl(2)	108.2 (8)
Torsion Angles			
Os-P(1)-C(21)-C(22)	-124.0 (4)	Os-P(1)-C(31)-C(32)	-148.6 (3)
Os-P(1)-C(41)-C(42)	-132.9 (5)	Os-P(2)-C(51)-C(52)	131.2 (5)
Os-P(2)-C(61)-C(62)	120.9 (4)	Os-P(2)-C(71)-C(72)	-28.4 (5)
N(1)-Os-C(1)-O(1)	-12 (10)	N(1)-N(2)-C(11)-C(12)	-6 (1)
Os-P(1)		Os-P(2)	
Os-N(1)-C(1)	-4.0 (4) <sup>a</sup>	Os-N(1)-C(1)	-168.4 (5) <sup>a</sup>

<sup>a</sup> Angle between the vector and the normal to the plane defined by the three atoms.

Although no close contacts result from these interactions, there are indications that the phosphine ligand associated with P(2) is more crowded than the other one. (1) Ring 6 has the largest P-C torsion angle of 59.1 (4)°; (2) the atom P(2) bends to a greater extent (11.6 (5)°) away from the phenyldiazo and carbonyl ligands and toward the hydrido ligand; and (3) the Os-P(2) bond length is the longer of the two by 0.008 (3) Å.

The solvent molecule seems to be partially disordered; the C-Cl distances, 1.58 (2) and 1.85 (2) Å, are unequal, but the average at 1.71 Å is near the expected value. The Cl(1)-

C(2)-Cl(2) angle at 108 (1)° is too small by about 5°. The dichloromethane sits in a cavity near rings 1 and 6, H(16)-H(1) = 2.33 and H(66)-H(2) = 2.48 Å. Indeed, there may be a weak interaction between H(2) and N(2) which are 2.38 Å apart.

There are no significant intermolecular interactions between molecules of the complex, the shortest distance being H(26)-H(62) = 2.49 Å.

**The Phenyldiazo Ligand.** The phenyldiazo ligand in this osmium complex assumes the singly bent geometry. The Os-N(1)-N(2) angle is almost linear (171.1 (6)°) and the N(1)-N(2)-C(11) angle is bent (118.5 (7)°), suggesting approximate sp hybridization about N(1) and sp<sup>2</sup> hybridization about N(2). The phenyldiazo ligand lies in an equatorial position and is almost coplanar with the trigonal plane defined by Os, N(1), and C(1); the angle between the trigonal plane and N(1), N(2), and C(11) is 3.0 (7)°. The torsion angle about N(2)-C(11) is 6 (1)°, and the angle between the least-squares plane through the diazo phenyl ring and the trigonal plane is 10.0 (6)°. The torsion angle about the C-N bond is about the same as those in other bis(triphenylphosphine)-aryldiazo complexes, [Fe(CO)<sub>2</sub>(NNPh)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sup>22</sup> at about 6° and RuCl<sub>3</sub>(NNTo)(PPh<sub>3</sub>)<sub>2</sub><sup>16</sup> at about 3°; however, the same torsion angle in a phenyldiazene complex which contains two trans triphenylphosphine ligands, [RuCl(CO)<sub>2</sub>(HNNPh)(PPh<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>]<sup>19</sup> is about 20°, owing to a close H...H interaction. It appears as though the torsion angle about the C-N bond is smaller in the osmium complex owing to the π conjugation of the Os-N-N-Ph network.

The most striking feature of the metrical details of the phenyldiazo ligand in this osmium complex is the unusually long Os-N(1) bond length at 1.867 (6) Å. This distance is significantly longer (~0.10 Å) than comparable distances in Ru and Os nitrosyl and aryldiazo complexes.<sup>16,37</sup> There is only one other example of an anomalously long Os-N distance, that of 1.89 (1) Å in [Os(CO)<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>].<sup>36</sup> Because the distances and angles involving the nitrosyl and carbonyl ligands were very similar in this osmium-nitrosyl complex, we suggested previously that the carbonyl and nitrosyl ligands might be disordered, thus accounting for the long Os-N distance.<sup>22,37</sup>

The N-C distance of 1.460 (10) Å is the longest such distance for a singly bent aryldiazo ligand, and the M-N-N (171.1 (6)°) and N-N-C (118.5 (7)°) angles are the smallest values yet observed. These angles and distances as well as the low value of ν(NN) all indicate the readiness of this singly bent, aryldiazo complex of Os(0) to go toward a doubly bent, aryldiazo complex of Os(II). It would be interesting to compare this hydrido-aryldiazo complex with the analogous chloro-aryldiazo complex which should have a greater tendency to go to the doubly bent form. A comparison of bond distances and angles for various aryldiazo ligands in Table VII reveals that the distances and angles for this osmium complex begin to approach those characteristic of doubly bent com-

Table VII. Some Bond Angles and Distances for Aryldiazo Ligands<sup>a</sup>

Compd	M-N	N-N	N-C	M-N-N	N-N-C	ν(NN)(ν) <sup>b</sup>
PtCl(p-NNC <sub>6</sub> H <sub>4</sub> F)(PEt <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	1.97 (3)	1.17 (3)	1.49 (3)	118 (2)	118 (2)	1461 (1511) <sup>j</sup>
[RhCl(NNPh)(ppp)] <sub>2</sub> [PF <sub>6</sub> ] <sup>d</sup>	1.954 (8)	1.17 (2)	1.43 (1)	125 (1)	119 (1)	1603 (1513) <sup>k</sup>
OsH(CO)(NNPh)(PPh <sub>3</sub> ) <sub>2</sub> <sup>e</sup>	1.867 (6)	1.211 (8)	1.460 (10)	171.1 (6)	118.5 (7)	1543 (1563) <sup>k</sup>
ReCl <sub>3</sub> (NNPh)(PPhMe <sub>2</sub> ) <sub>2</sub> <sup>f</sup>	1.77 (2)	1.23 (2)	1.43 (2)	173 (2)	119 (2)	~1535 (1585) <sup>l</sup>
Mo(HBPz <sub>3</sub> )(CO) <sub>2</sub> (NNPh) <sup>g</sup>	1.825 (4)	1.211 (6)	1.43 (2)	174.2 (1)	121.2 (2)	~1590 (1660) <sup>m</sup>
[Fe(CO) <sub>2</sub> (NNPh)(PPh <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ] <sup>h</sup>	1.702 (6)	1.201 (7)	1.404 (8)	179.2 (5)	124.2 (6)	1723 (1593) <sup>n</sup>
RuCl <sub>3</sub> (p-NNC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> <sup>i</sup>	1.784 (5)	1.158 (6)	1.376 (6)	171.9 (5)	137.1 (5)	1881 (1851) <sup>o</sup>

<sup>a</sup> Distances given in angstroms; angles given in degrees. Abbreviations: Ph, C<sub>6</sub>H<sub>5</sub>; Et, C<sub>2</sub>H<sub>5</sub>; Me, CH<sub>3</sub>; Pz, C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>; M, metal; ppp, PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPH<sub>2</sub>)<sub>3</sub>. <sup>b</sup> Frequency given in wave numbers (cm<sup>-1</sup>) for the phenyldiazo complex; see ref 10 and 16 for explanation of ν'. <sup>c</sup> Reference 11. <sup>d</sup> Reference 10. <sup>e</sup> This work. <sup>f</sup> Reference 20. <sup>g</sup> Reference 12. <sup>h</sup> Reference 22. <sup>i</sup> References 16 and 17. <sup>j</sup> Reference 19. <sup>k</sup> Reference 21. <sup>l</sup> This is the approximate value for the bis(phosphine)-ammine complex, ReCl<sub>3</sub>(NH<sub>3</sub>)(NNPh)(PPhMe<sub>2</sub>)<sub>2</sub>; R. Mason and B. L. Shaw, personal communication. <sup>m</sup> This is only approximate owing to resonance coupling with phenyl vibrational modes; see ref 6 and 8. <sup>n</sup> References 5 and 7. <sup>o</sup> Reference 3.

plexes. Indeed, preparing aryldiazo complexes with intermediate coordination geometries should be possible. Several trends are evident from Table VII. From top to bottom, the N–C distances decrease, and the M–N–N and N–N–C angles increase. Generally, the M–N distances decrease, but it is difficult to make detailed comparisons when different metals, charges, and coordination numbers are present. The Mo complex seems to have a somewhat long Mo–N distance, but it is the only complex without phosphine ligands present. The somewhat small Ru–N–N angle of 171.9 (5)° in the Ru complex seems to be caused by the steric crowding of the tolyldiazo ligand by the two triphenylphosphine ligands. Of special interest are the values of the N–N distances. At one extreme (Ru complex) we observe a shorter distance approaching an N–N triple-bond distance of 1.10 Å (from N<sub>2</sub>, PhN<sub>2</sub><sup>+</sup>),<sup>38</sup> and in the middle (Re complex) is found a longer distance approaching an N–N double-bond distance of 1.24 Å (from HN<sub>2</sub>H, PhN<sub>2</sub>Ph).<sup>39</sup> However, at the other extreme (Pt complex) we find shorter distances again for the doubly bent complexes. We believe that these changes in the N–N distances are real and chemically significant despite the marginal significance based on estimated standard deviations. The shortening of the N–O distance in bent nitrosyl ligands, as compared with linear nitrosyl ligands, has also been observed before.<sup>40</sup>

The trigonal-bipyramidal coordination geometry with the singly bent phenyldiazo ligand is consistent with our formulation of this complex as a phenyldiazoniumato complex of Os(0). The trend in the N–N stretching frequencies, as well as in the modified values ( $\nu'$ ),<sup>10,16</sup> parallels the changes in metrical parameters discussed above (see Table VII). As was discussed previously, the infrared spectra of OsH(CO)(NNPh)(PPh<sub>3</sub>)<sub>2</sub> contain three bands associated with  $\nu(\text{NN})$  which can be mathematically decoupled from interacting phenyl vibrational modes to obtain the true value of  $\nu(\text{NN})$  at 1543 cm<sup>-1</sup>.<sup>21</sup> This value, while still indicative of a singly bent coordination geometry for the aryldiazo ligand, is very low. Thus, we expect and indeed observe that this osmium complex undergoes reactions with nucleophiles such as HClO<sub>4</sub> which are characteristic of Os(0) complexes. In addition to its long Os–N bond length, this complex is the first carbonyl-containing aryldiazo complex whose value of  $\nu(\text{CO})$  is larger than that of the analogous nitrosyl complex.<sup>8</sup> The higher value of the C–O stretching frequency is usually taken as an indication of the better  $\pi$ -accepting properties of the other ligands in the coordination sphere, in this case the phenyldiazo ligand. If this is true, then it is consistent with the above structural and spectral (low  $\nu(\text{NN})$ ) data.

This osmium complex seems to be rather flexible owing to the lower coordination number (5) and the presence of the hydrido ligand which has reduced steric requirements. The coordination angles about the osmium atom illustrate not only this fact but also the absence of close intramolecular contacts and the high thermal motion of the diazo phenyl group. All the carbon atoms in this phenyl group, except for C(11) which is attached to N(2), are undergoing maximum thermal motion perpendicular to the plane of the ring. This is certainly caused by a significant amount of torsional vibration about the N(2)–C(11) bond combined with a small amount of wagging motion; Figure 2 clearly illustrates this anisotropic motion. All six carbon atoms in the phenyl group are coplanar; the largest deviation from the least-squares plane is less than its error. In two different models, (1) six individual anisotropic atoms and (2) one rigid body (C–C = 1.392 Å) with individual isotropic temperature parameters, the N(2)–C(11) distances were 1.460 (10) and 1.465 (10) Å, respectively. Although the first model is the better one, the angles and distances in the phenyldiazo ligand are not sensitive to the model.

OsH(CO)(NNPh)(PPh<sub>3</sub>)<sub>2</sub> undergoes a variety of reactions and is a useful intermediate for preparing other diazo and diazene complexes. The crystal structure of this complex is helpful in understanding its modes of reaction. It is anticipated that further synthetic, spectroscopic, and structural studies on aryldiazo and related complexes will help elucidate the nature of metal–nitrogen bonding and the reactions of ligands containing nitrogen–nitrogen multiple bonds.

**Acknowledgment.** This work was kindly supported by the National Science Foundation through the Northwestern University Materials Research Center. We are indebted to Matthey-Bishop, Inc., for the loan of the osmium used in this study. M. C. wishes to thank the National Research Council of Canada for a postdoctoral fellowship.

**Registry No.** OsH(CO)(NNPh)(PPh<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>, 56258-72-1.

**Supplementary Material Available.** The table of observed and calculated structure amplitudes 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 the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50374V-11-75.

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## Intercalative Stacking Interactions and Interligand Hydrogen Bonding in Metal-Purine Complexes. Crystal and Molecular Structure of (*N*-Salicylidene-*N'*-methylethylenediamine)(aquo)(9-methyladenine)copper(II) Nitrate Dihydrate

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Received June 30, 1975

AIC50455R

This report relates the synthesis and crystal structure of [(*N*-salicylidene-*N'*-methylethylenediamine)(aquo)(9-methyladenine)copper(II) nitrate], [(N<sub>2</sub>OC<sub>10</sub>H<sub>13</sub>)(H<sub>2</sub>O)(N<sub>5</sub>C<sub>6</sub>H<sub>7</sub>)Cu]NO<sub>3</sub>. The complex crystallizes from water as the dihydrate in the monoclinic system, space group *P2<sub>1</sub>/n*, with *a* = 12.765 (4) Å, *b* = 21.999 (19) Å, *c* = 7.776 (4) Å,  $\beta$  = 98.48 (3)°, *Z* = 4, *d*<sub>meas</sub> = 1.55 (1) g cm<sup>-3</sup>, *d*<sub>calcd</sub> = 1.56 g cm<sup>-3</sup>. Intensities for 4617 symmetry-averaged reflections were collected by diffractometer methods in the  $\theta$ -2 $\theta$  scan mode. Standard heavy-atom Patterson and Fourier techniques were used to solve the structure. Full-matrix least squares has led to a final *R* value of 0.075, a weighted *R* value of 0.055, and a goodness-of-fit value of 1.9. The primary coordination sphere about the copper center is approximately square pyramidal with the tridentate Schiff base chelate and N(7) of the 9-methyladenine ligand occupying the four equatorial coordination sites and a water molecule in the axial position, Cu-OH<sub>2</sub> distance = 2.353 (2) Å. The most unusual aspect of the structure is the interligand hydrogen bond which exists between the exocyclic amine at C(6) of the 9-methyladenine ligand and the equatorial oxygen atom, O(10), of the salicylidene portion of the Schiff base chelate. Typically, in related copper complexes, the exocyclic amino group forms a hydrogen bond to an axial substituent. The relationship between the Cu-N(7) bond length and the interligand interaction is discussed. The complex cations form columnar stacks along the short *c* axis via the *n*-glide symmetry operation. The intercalative stacking modes observed in the columnar stacks are compared to other known cases.

### Introduction

Stereoselective metal-ligand and ligand-ligand interactions can determine the binding site and stereochemistry of chelate-metal systems with purine and pyrimidine ligands. For example, the copper(II) complex of the tridentate ligand *N*-salicylidene-*N'*-methylethylenediamine has one equatorial site available for ligand attachment and presents to an incoming ligand both the exocyclic oxygen atom of the salicylidene ring and the *N*-methyl terminus of the ethylenediamine chain. The salicylidene oxygen is a potential hydrogen-bond acceptor site, while the *N*-methyl terminus is a potential hydrogen-bond donor group. In the complex (*N*-salicylidene-*N'*-methylethylenediamine)(theophyllinato)copper(II) [where theophyllinato is the monoanion of 1,3-dimethyl-2,6-dioxopurine] the metal binding site is N(7) of the imidazole ring.<sup>1</sup> The complex shows a strong interligand hydrogen bond between the exocyclic carbonyl oxygen at C(6) of the purine ring and the terminal secondary amine of the ethylenediamine group. In the related complex (*N*-salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II) nitrate the heterocyclic ring nitrogen, N(3), of the pyrimidine was bound to the metal.<sup>2</sup> Furthermore, the exocyclic carbonyl

oxygen atom at C(2) of the pyrimidine ring formed a weak, but apparently specific, interaction with the copper center via one of the open axial positions of the basic square-planar coordination sphere. The complex cation also exhibits a weak interligand hydrogen bond to the *N*-methylethylenediamine terminus of the Schiff base chelate via the same carbonyl oxygen at C(2).

As a continuation of our studies of specificity associated with exocyclic groups, we have prepared and studied the complex formed between 9-methyladenine and the (*N*-salicylidene-*N'*-methylethylenediamine)copper(II) moiety. This particular complex was chosen for several reasons. We wished to obtain a set of complexes of one multidentate chelate moiety which would afford bonding models for the three common nucleosides (adenosine, guanosine, cytidine) which are expected to interact with copper complexes in the nucleic acids. (The binding of uridine and thymidine is much less important.<sup>3</sup>) The theophyllinato and the cytosine complexes are models for guanosine and cytidine, respectively. The 9-methyladenine complex would then provide information concerning the binding mode of adenosine as both molecules have substituents at N(9). It was of additional interest to us that the complex precursor,