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Comparison of Linear Nitrosyl and Singly Bent Aryldiazo Complexes of Ruthenium. Structures of $RuCl_3(NO)(P(C_6H_5)_3)_2$ and $RuCl_3(p\text{-}NNC_6H_4CH_3)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

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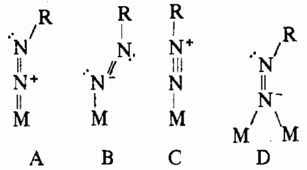
The structures of $RuCl_3(NO)(P(C_6H_5)_3)_2$ and $RuCl_3(p\text{-}NNC_6H_4CH_3)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$ have been determined crystallographically. Both complexes possess a similar pseudooctahedral geometry with trans phosphine ligands and meridional chloro ligands. The short Ru–N and N–X (X = O, N) distances suggest that both nitrosyl and aryldiazo ligands are good π acceptors; however, subtle but distinct differences in the two ligands suggest that NO is the better π acceptor. The much greater steric bulkiness of the aryldiazo ligand has a pronounced effect on the intramolecular interactions within the complex and on the three-dimensional packing of the complex in the solid state. Both Ru–N–X angles are essentially linear. The N(1)–N(2)–C(phenyl) angle at 137.1 (5)° in the diazo complex is unusually large. The Ru–Cl(trans to N) distances compared with the Ru–Cl(trans to Cl) distances are shortened by 0.041 (3) Å in the nitrosyl complex and by 0.008 (3) Å in the diazo complex. Both compounds are considered to be Ru(II) complexes of NO^+ or $NNAr^+$, with the respective ligands acting as three-electron donors. The nitrosyl complex crystallizes from dichloromethane–methanol as solvent-free crystals in space group C_{2h}^6-$I2/a$ with $a = 15.877$ (3) Å, $b = 9.540$ (2) Å, $c = 22.326$ (4) Å, $\beta = 102.79$ (1)°, and $Z = 4$. Each molecule has imposed C_2 symmetry. On the basis of 2671 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by full-matrix, least-squares methods to $R = 0.058$ and $R_w = 0.068$. Some important molecular parameters are Ru–N = 1.737 (7) Å, N–O = 1.142 (8) Å, and Ru–N–O = 180.0°. The tolyldiazo complex crystallizes from dichloromethane as solvated crystals in space group C_{2h}^5-$P2_1/c$ with $a = 12.406$ (8) Å, $b = 18.421$ (13) Å, $c = 18.565$ (13) Å, $\beta = 93.05$ (1)°, and $Z = 4$. The molecule has no imposed symmetry, but approximates C_s symmetry. On the basis of 5100 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by full-matrix, least-squares methods to $R = 0.058$ and $R_w = 0.067$. Some important molecular parameters in the diazo complex are Ru–N(1) = 1.784 (5) Å, N(1)–N(2) = 1.158 (6) Å, N(2)–C(phenyl) = 1.376 (6) Å, and Ru–N(1)–N(2) = 171.9 (5)°. Both structures consist of discrete monomeric molecules of the respective complex. The values of ν(NO) and ν(NN) for these and other nitrosyl and aryldiazo complexes are discussed, and some empirical rules are suggested for distinguishing between bent and linear nitrosyl ligands and between doubly bent and singly bent aryldiazo ligands on the basis of the N–O and N–N stretching frequencies. The syntheses of $[M(NO)(diphos)_2][PF_6]_2$ (M = Rh, Ir) are reported.

Introduction

Nitrosyl and aryldiazo (aryldiazenyl) ligands, as well as others which contain metal–nitrogen multiple bonds, have been of great interest in recent years because of their amphoteric nature and their close relationship to dinitrogen ligands. Structural and synthetic studies have shown the reaction chemistry of these ligands to be varied and interesting.[1–6] Indeed, nitrosyl and aryldiazo ligands have been shown to exist in both linear and bent forms corresponding to three-electron and one-electron donor ligands, respectively. Much of the reaction chemistry points to this dichotomy too. Whereas some nitrosyl complexes, such as $RuCl(NO)(bpy)^{2+}$ [7,8] and $IrCl_3(NO)(PPh_3)_2^+$,[9] have high values of ν(NO) and react as electrophiles with $PhNH_2$ and EtOH, other nitrosyl complexes, such as $OsCl(CO)(NO)(PPh_3)_2$[10] and $ReCl(NO)_2(PPh_3)_2$,[11] have lower values of ν(NO) and react as nucleophiles with HCl. Aryldiazo complexes seem to show similar types of reactions[12,13] with the additional possibilities of ortho metalation[14,15] of the aryl group and N_2 elimination.[12] Especially noteworthy are the preparations of alkyl, acyl, and aroyldiazo ligands from coordinated dinitrogen in rhenium, molybdenum, and tungsten complexes.[16,17]

The varied coordination geometries attainable by nitrosyl and diazo ligands indicate the versatility of these ligands. Indeed, three of four modes of coordination described by A–D



A B C D

have been clearly identified structurally for both ligands.[4,18–21] Only the totally linear geometry (C) has not been unambiguously observed for both nitrosyl and aryldiazo ligands.

The present study of the structures of the title compounds, $RuCl_3(NO)(PPh_3)_2$ and $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2 \cdot CH_2Cl_2$, was undertaken to provide a direct comparison of the bonding of linear nitrosyl and singly bent aryldiazo ligands in identical chemical environments. A similar comparison of bent nitrosyl and doubly bent aryldiazo ligands has been made.[20,22] Preliminary results of the tolyldiazo structure were reported earlier.[23] Subsequently, Eisenberg and coworkers published the determination of the structure of the tolyldiazo complex as the acetone solvate.[24] We are now able to compare our data for the tolyldiazo structure with theirs and also able to compare the results for the nitrosyl complex with an analogous one which contains a different phosphine, PPh_2Me.[25] To date, only three other complexes which contain singly bent aryldiazo ligands attached to Mo,[19] Re,[26] and Fe[27] have been studied structurally.

In the past, the distinction between linear (A) and bent (B) geometries in mononuclear nitrosyl (and aryldiazo) complexes was made by means of crystallographic studies. Although the values of ν(NO) derived from vibrational spectroscopy were thought to be correlated with the geometry of the nitrosyl ligand (large ν(NO), linear NO; small ν(NO), bent NO), there was a large region of overlap in the range 1600–1720 cm^{-1} which contained N–O stretching frequencies for both linear and bent nitrosyl ligands. Hence, this method of distinguishing between nitrosyl geometries has been held unreliable. We propose here an empirically derived method for modifying the observed N–O and N–N stretching frequencies in nitrosyl and aryldiazo complexes so that the region of overlap is greatly reduced, and the presence of linear or bent nitrosyl and aryldiazo ligands can be determined with much greater reliability from the modified stretching frequency.

Experimental Section

Crystal Preparation. The ruthenium nitrosyl complex was prepared by two different literature methods.[28,29] However, after dozens of attempts no crystals of suitable size could be prepared owing to the very low solubility of this complex in a variety of common laboratory solvents with which it does not react. Finally, a third method of preparation was devised, reaction 1. Using concentrated methanolic

$$\mathrm{RuCl_2(PPh_3)_3} + t\text{-}\mathrm{BuONO} + \mathrm{H_2SO_4} + \mathrm{LiCl} \xrightarrow[\text{ethanol}]{\text{refluxing}} \mathrm{RuCl_3(NO)(PPh_3)_2} \qquad (1)$$

HCl instead of sulfuric acid and lithium chloride, this reaction was carried out without stirring at room temperature in a threefold amount of solvent (dichloromethane–methanol, 90:10 by volume, instead of pure ethanol) over a period of 2 days. Sufficiently large crystals were thus prepared and grown in situ. These crystals had the same elemental analyses, melting point, and infrared spectrum as the bulk samples prepared before. Anal. Calcd for $C_{36}H_{30}Cl_3NOP_2Ru$: C, 56.74; H, 3.97; N, 1.84; Cl, 13.96. Found: C, 56.81; H, 3.99; N, 1.77; Cl, 13.99. The amber, air-stable platelets of suitable quality and size were mounted in air on glass fibers.

The tolyldiazo and phenyldiazo complexes were prepared as the acetone solvates by the published method.[13] $RuCl_2(PPh_3)_4$ was used as starting material instead of the analogous tris(phosphine) complex only because it was conveniently available at the time. Even after several recrystallizations, no crystal without unacceptably high mosaicity could be found. Because of its enhanced solubility, the tolyldiazo complex was recrystallized several times from dichloromethane by evaporation to yield beautiful amber prisms of satisfactory quality and size. Infrared and NMR spectra showed the presence of dichloromethane and complete absence of acetone. Anal. Calcd for $C_{44}H_{39}Cl_5N_2P_2Ru$: C, 56.46; H, 4.20; N, 2.99; Cl, 18.94; P, 6.62; Ru, 10.80. Found: C, 56.71; H, 4.31; N, 2.70; Cl, 18.54; P, 6.81; Ru, 10.82. The crystals were mounted as before. Elemental analyses were performed by Meade Microanalytical Laboratory, Amherst, Mass., and by H. Beck of Northwestern's Analytical Services Laboratory. Infrared spectra were recorded in hexachlorobutadiene and Nujol mulls using a Perkin-Elmer 337 double-beam spectrometer with a scale-expanding unit attached. The spectra were calibrated using a polystyrene film. The NMR spectra were recorded using a Perkin-Elmer R20B spectrometer at ambient temperatures with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Although Laing et al.[13] formulated the tolyldiazo complex as a hemisolvate, the chloride analyses and NMR spectra of our crystals showed the complex-to-solvent ratio in the freshly recrystallized samples to vary from 1:1.05 to 1:0.85. Samples of the dichloromethane solvate appeared to desolvate slowly (about 10% per month). There was no obvious deterioration of crystal quality during data collection.

Trichloronitrosylbis(triphenylphosphine)ruthenium. In a stoppered reaction vessel 2.30 g of $RuCl_2(PPh_3)_3$, 1.00 g of LiCl, and 1.8 ml of *tert*-butyl nitrite were stirred at room temperature for 1 hr in 150 ml of absolute ethanol which contained 1.0 ml of 96% sulfuric acid. During this time the dark brown mixture became yellow. The mixture was then refluxed for 15 min, cooled, and filtered. The product was washed with methanol and dried under vacuum; yield 89% of a yellow microcrystalline powder; ν(NO) 1881 cm^{-1}. The same reaction performed on one-tenth scale using *n*-butyl nitrite-^{15}N yielded the isotopically substituted product; ν(NO) 1848 cm^{-1}. Anal. Calcd for $C_{36}H_{30}Cl_3NOP_2Ru$: C, 56.74; H, 3.97; N, 1.84; Cl, 13.96. Found: C, 56.59; H, 3.99; N, 1.88; Cl, 13.71.

Nitrosylbis(1,2-bis(diphenylphosphino)ethane)iridium(2+) Hexafluorophosphate. In 10 ml of acetone, 0.30 g of $[Ir(diphos)_2][PF_6]$ and 0.10 g of $[NO][PF_6]$ were stirred together at room temperature for 5 min. The reaction mixture changed from orange to dark yellow. Forty milliliters of diethyl ether was slowly added. The product was filtered, washed with ether, and dried under vacuum; yield 76% of golden yellow crystals; ν(NO) 1709 cm^{-1}. The carbonyl adduct, $[Ir(CO)(diphos)_2][PF_6]$, was used as starting material with equal success in this reaction. Anal. Calcd for $C_{52}H_{48}F_{12}IrNOP_6$: C, 47.72; H, 3.70; N, 1.07. Found: C, 48.01; H, 3.82; N, 1.01.

Nitrosylbis(1,2-bis(diphenylphosphino)ethane)rhodium(2+) Hexafluorophosphate. This compound was prepared exactly as the analogous iridium complex except that the yellow rhodium complex $[Rh(diphos)_2][PF_6]$ was used; yield 79% of green crystals; ν(NO) 1748 cm^{-1}. The same reaction was performed on half-scale using equivalent amounts of *n*-butyl nitrite-^{15}N and HPF_6 (75% yield) or $Na^{15}NO_2$ and HPF_6 (40% yield) to give the isotopically substituted product; ν(NO) 1717 cm^{-1}. Anal. Calcd for $C_{52}H_{48}F_{12}NOP_6Rh$: C, 51.21; H, 3.97; N, 1.15. Found: C, 51.32; H, 3.95; N, 1.02.

Table I. Summary of Crystal Data, Intensity Collection, and Refinement

Compd	$RuCl_3(NO)(P(C_6H_5)_3)_2$	$RuCl_3(p\text{-}N_2C_6H_4\text{-}CH_3)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$
Formula	$C_{36}H_{30}Cl_3NOP_2Ru$	$C_{44}H_{39}Cl_5N_2P_2Ru$
Formula wt	762.02	936.10
a, Å	15.877 (3)	12.406 (8)
b, Å	9.540 (2)	18.421 (13)
c, Å	22.326 (4)	18.565 (13)
β, deg	102.79 (1)	93.05 (1)
V, Å^3	3298	4237
Z	4	4
Density, g/cm^3	1.535 (calcd); 1.53 (1) (exptl)	1.467 (calcd); 1.45 (1) (exptl)
Space group	$C_{2h}{}^6$-$I2/a$	$C_{2h}{}^5$-$P2_1/c$
Crystal dimensions, mm	0.34 × 0.33 × 0.05	0.75 × 0.51 × 0.10
Crystal vol, mm^3	0.0067	0.0306
Crystal shape	Platelet with large {001} faces and {110} edge faces	Platelet with large {100} faces and {011} edge faces
Radiation	Mo Kα_1 (λ 0.709300 Å), monochromatized from (002) face of mosaic graphite	Mo Kα_1 (λ 0.709300 Å), monochromatized from (002) face of mosaic graphite
Temp, °C	21	22
μ, cm^{-1}	8.33	7.14
Transmission factors	0.817–0.958	0.720–0.929
Receiving aperture	5.0 mm wide × 4.5 mm high, 32 cm from crystal	6.0 mm wide × 4.5 mm high, 32 cm from crystal
Takeoff angle, deg	2.0	2.2
Scan speed	2.0° in 2θ/min	2.0° in 2θ/min
Scan range	1.05° below Kα_1 to 0.95° above Kα_2	1.0° below Kα_1 to 0.9° above Kα_2
Background counting	10 sec for $2\theta < 30°$; 20 sec thereafter	10 sec for $2\theta < 39°$; 20 sec thereafter
2θ limits, deg	3.0–54.0	3.0–47.5°
Final no. of variables	75	193
Unique data used ($F_o{}^2 > 3\sigma(F_o{}^2)$)	2671	5100
Error in observation of unit wt, electrons	2.18	2.65
R	0.058	0.058
R_w	0.068	0.067

Crystallographic Data. Preliminary film data showed the nitrosyl crystal to belong to the monoclinic system with extinctions (*hkl*, *h* + *k* + *l* odd; *h*0*l*, *h* odd, *l* odd; 0*k*0, *k* odd) characteristic of the centrosymmetric space group $C_{2h}{}^6$-$I2/a$ and the noncentric space group $C_s{}^4$-Ia. The centrosymmetric space group was shown to be the correct one on the basis of the following results: (a) the successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices; (b) the clear and distinct location of all 15 unique hydrogen atoms in difference Fourier syntheses; (c) the statistical equivalence of the intensities of 151 pairs of reflections related by a center of inversion. On the basis of a least-squares analysis[30] of the angular positions of 18 hand-centered reflections in diverse regions of reciprocal space (in the range 28° > 2θ > 20°), accurate unit cell dimensions were determined. The tolyldiazo crystal also belongs to the monoclinic system with extinctions (*h*0*l*, *l* odd; 0*k*0, *k* odd) characteristic of the centrosymmetric space group $C_{2h}{}^5$-$P2_1/c$. In a similar manner, 16 reflections were used to obtain accurate unit cell dimensions for this crystal. See Table I for pertinent crystal information and details of data collection for both crystals. Both crystals displayed acceptable mosaicities for the θ-2θ scan technique. Data collection was carried out on a Picker four-circle diffractometer. 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. For the nitrosyl crystal, all six were found to remain constant within counting statistics during the entire data collection. For the tolyldiazo crystal, all six were found to decrease uniformly and linearly by 1–3% during the course of data collection. The observed intensities were corrected for this small, apparently isotropic crystal decomposition. Both data sets were processed in the usual way with $\sigma(F_o{}^2)$

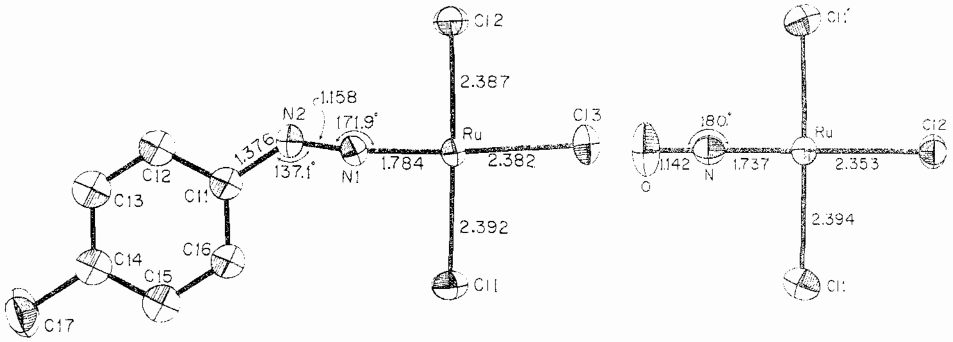


Figure 1. The coordination spheres with some bond distances and angles for $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2\cdot CH_2Cl_2$ and $RuCl_3(NO)(PPh_3)_2$. The triphenylphosphine ligands and solvent molecules have been omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

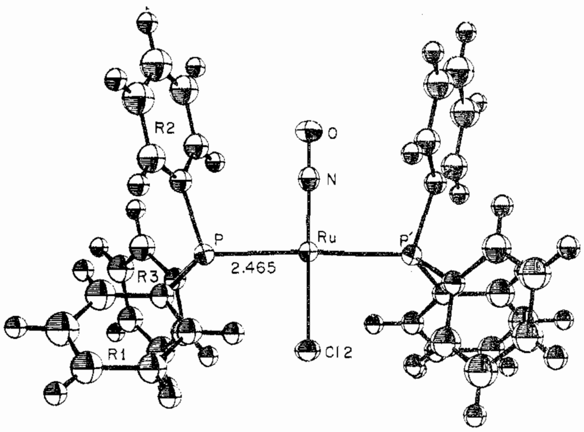


Figure 2. A molecule of $RuCl_3(NO)(PPh_3)_2$ with Cl(1) and Cl(1)' missing. The phenyl rings are appropriately numbered. Vibrational ellipsoids are drawn at the 50% probability level except for the hydrogen atoms whose isotropic thermal parameters were reduced by one-half. The molecule has imposed C_2 symmetry with Ru, N, O, and Cl(2) lying on the symmetry axis.

calculated using a value of 0.04 for p.[30] Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. An absorption correction was applied to both data sets using Gaussian integration.[31]

Structure Refinement. The structures were solved using Patterson syntheses to locate the ruthenium atoms. Subsequent refinements and difference Fourier syntheses revealed the presence of all atoms in both structures including all hydrogen atoms except the two hydrogen atoms of the CH_2Cl_2 solvent in the tolyldiazo structure. The structures were refined using full-matrix, least-squares techniques. 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 the usual sources.[32] The anomalous dispersion terms for Ru, Cl, and P were included in F_c.[33] All phenyl groups were refined as rigid, planar bodies with a constant and uniform C–C distance of 1.397 Å and with isotropic thermal parameters. 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 1.00 Å, the CCH angles were assumed to be 120.0°, and the thermal parameter of a hydrogen atom was assumed to be equal to that of the carbon atom to which it was attached.

The nitrosyl structure converged to $R = 0.058$ and $R_w = 0.068$ while the tolyldiazo structure converged to $R = 0.058$ and $R_w = 0.067$. A comparison of $|F_c|$ and $|F_o|$ for the stronger reflections shows no obvious need for an extinction correction in either structure. In neither structure were there trends of the quantity $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, diffractometer setting angles, or Miller indices. Final difference Fourier syntheses revealed nothing significant in either structure. In the nitrosyl structure the two highest peaks were residuals near Ru (1.2 e/Å^3) and P (1.0 e/Å^3). In the tolyldiazo complex, the four highest peaks (0.9–1.4 e/Å^3) were residuals near the solvent. Otherwise, the only other residuals (0.5–0.7 e/Å^3) in both structures were near the rigid phenyl groups. For both structures, a typical carbon atom had a height of 3.1 e/Å^3.

The final positional and thermal parameters of atoms and groups appear in Tables II and III, and root-mean-square amplitudes of vibration are given in Table IV. A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[34]

Discussion

Description of the Nitrosyl Structure. The structure of $RuCl_3(NO)(PPh_3)_2$ consists of discrete, well-separated monomers. The labeling scheme for this complex, together with some bond distances and angles in the inner coordination sphere, is shown in Figures 1 and 2. A stereodrawing of the unit cell is shown in Figure 3. The complex has pseudooctahedral geometry with trans phosphine ligands, meridional chloro ligands, and a linear nitrosyl ligand. The three mutually perpendicular coordination planes are well defined. There are no significant intermolecular contacts, the shortest being H(14)–H(22) = 2.48 Å, H(15)–H(22) = 2.33 Å, H(32)–H(25) = 2.41 Å, and H(33)–H(25) = 2.42 Å.

This ruthenium nitrosyl complex, $RuCl_3(NO)(PPh_3)_2$, is isomorphous with $OsCl_3(NH_3)(PPh_3)_2$[35] and it has the same space group and unit cell dimensions as several similar square-pyramidal, five-coordinate complexes, $ReCl_2N(PPh_3)_2$,[30] $IrCl_2(NO)(PPh_3)_2$,[36] and $IrI(CH_3)(NO)(PPh_3)_2$[37] (hence the choice here of the $I2/a$ setting, rather than the conventional $C2/c$ setting). All complexes have only moderate to very poor solubility in ordinary laboratory solvents, all crystallize without solvent of crystallization, and apparently all have an imposed C_2 axis (sometimes with accompanying disorder) in the solid state. The packing of the two bulky triphenylphosphine ligands which are trans to each other seems

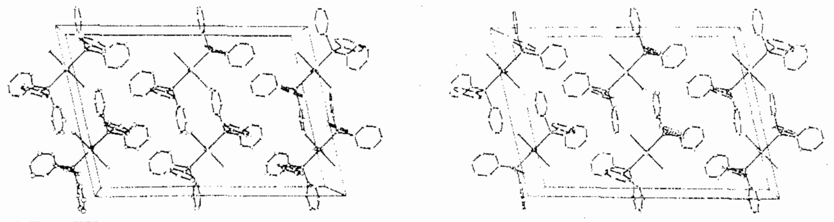


Figure 3. A stereodrawing of a unit cell of $RuCl_3(NO)(PPh_3)_2$. The x axis is almost vertical, the y axis is perpendicular to the paper coming toward the reader, and the z axis is horizontal to the right. Vibrational ellipsoids are drawn at the 20% level.

Table II. Final Parameters for $RuCl_3(NO)(P(C_6H_5)_3)_2$ and $RuCl_3(p\text{-}N_2C_6H_4CH_3)(P(C_6H_5)_3)_2\cdot CH_2Cl_2$

Atom	x[a]	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru[c]	$^1/_4$	0.16507 (7)	0	0.00216 (3)	0.00499 (7)	0.00099 (1)	0	0.00018 (1)	0
Cl(1)	0.13691 (10)	0.16146 (18)	0.05528 (7)	0.00331 (7)	0.01064 (19)	0.00166 (3)	−0.00081 (10)	0.00078 (4)	0.00018 (7)
Cl(2)	$^1/_4$	0.41174 (20)	0	0.00341 (9)	0.00567 (22)	0.00159 (5)	0	0.00052 (5)	0
P	0.36469 (9)	0.17073 (15)	0.09460 (6)	0.00229 (6)	0.00548 (15)	0.00107 (3)	0.00012 (8)	0.00014 (3)	−0.00011 (5)
O	$^1/_4$	−0.1367 (6)	0	0.0050 (4)	0.0056 (8)	0.0029 (2)	0	−0.0008 (2)	0
N	$^1/_4$	−0.0170 (7)	0	0.0018 (3)	0.0076 (9)	0.0014 (2)	0	0.0002 (2)	0
Ru[d]	0.08332 (4)	0.47661 (3)	0.22291 (2)	0.00400 (4)	0.00133 (2)	0.00140 (2)	−0.00004 (2)	0.00004 (2)	−0.00016 (1)
Cl(1)	0.05870 (14)	0.53168 (9)	0.10652 (8)	0.00685 (13)	0.00229 (5)	0.00184 (5)	0.00016 (7)	0.00006 (6)	0.00041 (4)
Cl(2)	0.09826 (13)	0.41825 (9)	0.33781 (8)	0.00617 (12)	0.00217 (5)	0.00181 (5)	0.00039 (6)	0.00006 (6)	0.00024 (4)
Cl(3)	0.15204 (13)	0.58366 (8)	0.28084 (9)	0.00527 (12)	0.00186 (5)	0.00259 (5)	−0.00037 (6)	0.00005 (6)	−0.00076 (4)
Cl(4)	0.5060 (6)	0.1718 (4)	0.1812 (5)	0.0372 (11)	0.0172 (5)	0.0227 (6)	−0.0068 (6)	0.0181 (7)	−0.0100 (5)
Cl(5)	0.5969 (6)	0.1249 (4)	0.0611 (3)	0.0423 (11)	0.0228 (6)	0.0059 (2)	−0.0097 (7)	0.0026 (4)	−0.0015 (3)
P(1)	0.26614 (13)	0.44867 (9)	0.18959 (8)	0.00429 (11)	0.00181 (5)	0.00167 (5)	0.00018 (6)	0.00018 (6)	−0.00010 (4)
P(2)	−0.10113 (13)	0.51295 (8)	0.24408 (8)	0.00410 (11)	0.00160 (5)	0.00159 (5)	0.00004 (6)	0.00000 (6)	−0.00006 (4)
N(1)	0.0359 (4)	0.3927 (3)	0.1853 (3)	0.0045 (4)	0.0017 (2)	0.0015 (2)	0.0000 (2)	0.0000 (2)	−0.0003 (1)
N(2)	0.0066 (4)	0.3350 (3)	0.1691 (3)	0.0063 (4)	0.0016 (2)	0.0021 (2)	−0.0006 (2)	−0.0002 (2)	−0.0002 (1)
C(17)	−0.1512 (7)	0.1868 (4)	−0.0830 (4)	0.0105 (8)	0.0032 (3)	0.0034 (3)	−0.0003 (4)	−0.0006 (4)	−0.0016 (2)
C(1)	0.5776 (17)	0.1249 (11)	0.1505 (11)	0.0311 (29)	0.0111 (11)	0.0115 (11)	0.0098 (15)	0.0030 (14)	−0.0018 (9)

Group	x_c[e]	y_c	z_c	δ	ϵ	η
1[c]	0.3377 (2)	0.3489 (3)	0.2113 (1)	1.215 (3)	2.814 (2)	1.089 (3)
2	0.3885 (2)	−0.1530 (3)	0.1350 (1)	−2.012 (6)	2.011 (3)	0.550 (6)
3	0.5510 (2)	0.2938 (3)	0.0872 (1)	−2.680 (2)	−2.943 (3)	−2.912 (3)
1[d]	−0.0703 (2)	0.2633 (2)	0.0455 (1)	−0.163 (3)	2.551 (2)	−1.838 (3)
11	0.2434 (2)	0.3222 (2)	0.0702 (2)	−3.187 (4)	−2.324 (2)	−1.473 (4)
12	0.4329 (2)	0.3901 (2)	0.3157 (2)	0.588 (4)	−2.423 (2)	1.217 (4)
13	0.4080 (2)	0.5728 (2)	0.1145 (2)	0.807 (3)	−2.974 (3)	−0.494 (3)
21	−0.1803 (2)	0.5237 (2)	0.4060 (2)	−1.217 (3)	−2.899 (2)	1.792 (3)
22	−0.2483 (3)	0.4000 (2)	0.1509 (2)	0.017 (5)	2.252 (3)	−2.132 (5)
23	−0.1853 (2)	0.6720 (2)	0.1947 (1)	1.889 (2)	−2.987 (3)	−0.233 (3)

[a] Estimated standard deviations of the least significant figure are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] For $RuCl_3(NO)(PPh_3)_2$. [d] For $RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2\cdot CH_2Cl_2$. [e] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers; the angles δ, ϵ, and η (radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 793 (1965). Three phenyl groups (11, 12, 13) are attached to P(1), and three others (21, 22, 23) are attached to P(2); group 1 belongs to the tolyldiazo ligand.

to govern the solid-state structure of these complexes. In fact, the *I*2/*a* (*C*2/*c*) space group with four formula units per unit cell is probably the preferred one for such neutral, square-pyramidal or pseudooctahedral, bis(triphenylphosphine) complexes when the coordination plane perpendicular to the P–P vector contains three or four ligands of low steric bulk which will not cause unusual intermolecular interactions or cause the phosphine ligands to distort excessively by rotation about the P–C bonds. The compound $Os(CO)_3(PPh_3)_2$[38] and its Ru analogue are trigonal bipyramids and crystallize in a trigonal space group. The compound $IrCl(CO)_2(PPh_3)_2$[39] is trigonal bipyramidal and crystallizes with solvent of crystallization in space group $P2_1/c$.

The metal–ligand distances fall near the expected values (see Table V). The Ru–P distance at 2.465 (1) Å is one of the longest observed for six-coordinate, ruthenium complexes containing two trans triphenylphosphine ligands. Such distances usually fall in the range 2.41–2.44 Å.[40] The Ru–N distance of 1.737 (7) Å is near the expected metal–nitrogen double-bond distance of 1.75 (3) Å in Ru and Os complexes which contain linear nitrosyl ligands.[41] The Ru–Cl(1) distance at 2.394 (2) Å is essentially the same as other such distances at 2.39 Å in ruthenium(II) phosphine complexes when the nonbridging chloro ligand is trans to another chloro ligand.[40] In phosphine complexes of Ru(III) and Os(III) these distances shorten by about 0.03 Å. The Ru–Cl(2) at 2.353 (2) Å is noticeably shortened as a result of its trans disposition to the nitrosyl ligand.

As noted earlier, the conformation of the bulky triphenylphosphine ligands governs the intramolecular geometry. Even in the absence of other bulky ligands, there is evidence of some steric crowding in the ruthenium nitrosyl complex. The torsion angles about the P–C bonds are normal for ring 2 and ring 3, but ring 1 has an exceptionally small torsion angle of 2.4 (3)° indicating that it is almost perpendicular to the Ru, N, Cl(1), C(1)′, Cl(2) coordination plane. Indeed, it is wedged between Cl(1) and Cl(2) causing Cl(1) to move toward P′ while increasing ∠Cl(1)–Ru–P and decreasing ∠Cl(1)–Ru–P′ by about 3°. Ring 1 cannot rotate appreciably about its P–C bond without approaching too close to either Cl(1) and Cl(2) or the ortho hydrogen atoms on the other two rings. Rings 2 and 3 rotate in the same direction about their respective P–C bonds. Had they rotated in different directions, the phosphine would have possessed the "mirror" geometry; however, such a rotation would have significantly reduced the distance between H(26) and H(36) at 2.34 Å, which already is the shortest nonbonded interaction in the structure. As can be seen from Figure 2, the oxygen atom lies between the faces of ring 2 and ring 2′. The nitrosyl ligand finds itself in a far less crowded situation than Cl(2) which is held in a cage composed of H(16), H(16)′, H(32), and H(32)′. Fortunately, the cage is somewhat symmetric and Cl(2) remains on the twofold axis in contrast to the nitrogen atom in $IrCl_2(NO)(PPh_3)_2$ which is located in the same relative position but is pushed off the C_2 axis. Despite the more crowded location around Cl(2), the phosphine ligands bend *toward* Cl(2) and away from the nitrosyl group by about 1.2° indicating the greater effective steric bulk of the nitrosyl ligand. It is difficult to say, however, whether this greater effective steric bulk simply results from the nearness of the nitrosyl ligand to the metal or results from the inherently greater size of the nitrosyl ligand owing to an extensive π-bonding interaction with the metal. In any case, the bulkiness of the nitrosyl ligand is underscored by the structural data for two similar systems, $RuCl_3(NO)(PPh_2Me)_2$[25] and $OsCl_3(NH_3)(PPh_3)_2$.[35] The less bulky phosphine ligands in the ruthenium complex bend away from the nitrosyl ligand by an even greater amount (4.1°). In the osmium complex, which

Table III. Derived Positional and Thermal Parameters for Ring Atoms

	Carbon				Hydrogen		
Atom[a]	*x*	*y*	*z*	*B*[b]	*x*	*y*	*z*
C(11)[c]	0.3473 (2)	0.2707 (4)	0.1604 (2)	2.52 (10)			
C(12)	0.4118 (2)	0.2680 (4)	0.2142 (2)	3.99 (13)	0.466	0.210	0.216
C(13)	0.4023 (2)	0.3462 (5)	0.2652 (2)	4.70 (15)	0.451	0.342	0.304
C(14)	0.3281 (3)	0.4271 (5)	0.2623 (2)	3.95 (13)	0.324	0.481	0.301
C(15)	0.2636 (2)	0.4298 (4)	0.2085 (2)	3.33 (12)	0.212	0.487	0.209
C(16)	0.2731 (2)	0.3516 (4)	0.1575 (2)	2.75 (10)	0.227	0.355	0.120
C(21)	0.3827 (3)	−0.0106 (3)	0.1202 (2)	2.32 (9)			
C(22)	0.3555 (3)	−0.0588 (4)	0.1719 (2)	3.48 (12)	0.332	0.008	0.198
C(23)	0.3613 (3)	−0.2012 (4)	0.1867 (2)	4.40 (15)	0.342	−0.236	0.224
C(24)	0.3943 (3)	−0.2955 (3)	0.1498 (2)	4.66 (15)	0.398	−0.398	0.160
C(25)	0.4215 (3)	−0.2473 (4)	0.0981 (2)	3.99 (14)	0.445	−0.315	0.072
C(26)	0.4157 (3)	−0.1049 (4)	0.0833 (2)	3.07 (11)	0.435	−0.071	0.046
C(31)	0.4706 (2)	0.2362 (4)	0.0885 (2)	2.42 (9)			
C(32)	0.4767 (2)	0.3763 (4)	0.0718 (2)	3.85 (13)	0.423	0.435	0.060
C(33)	0.5572 (3)	0.4339 (3)	0.0704 (2)	4.40 (15)	0.561	0.534	0.058
C(34)	0.6315 (2)	0.3514 (4)	0.0859 (2)	3.65 (12)	0.689	0.392	0.085
C(35)	0.6254 (2)	0.2113 (4)	0.1026 (2)	3.99 (13)	0.678	0.152	0.114
C(36)	0.5449 (2)	0.1537 (3)	0.1039 (2)	3.47 (12)	0.540	0.054	0.116
C(11)[d]	−0.0311 (3)	0.3002 (2)	0.1071 (2)	2.78 (12)			
C(12)	−0.0639 (4)	0.2279 (2)	0.1121 (2)	3.37 (13)	−0.060	0.202	0.160
C(13)	−0.1031 (4)	0.1910 (2)	0.0504 (2)	3.70 (14)	−0.127	0.139	0.054
C(14)	−0.1096 (4)	0.2264 (2)	−0.0162 (2)	3.35 (13)			
C(15)	−0.0768 (4)	0.2987 (2)	−0.0212 (2)	3.60 (13)	−0.082	0.324	−0.069
C(16)	−0.0376 (4)	0.3356 (2)	0.0405 (2)	2.99 (12)	−0.015	0.387	0.037
C(111)	0.2581 (4)	0.3769 (2)	0.1220 (2)	2.73 (11)			
C(112)	0.2538 (4)	0.3945 (2)	0.0487 (2)	3.48 (13)	0.260	0.447	0.033
C(113)	0.2391 (4)	0.3398 (2)	−0.0031 (2)	4.50 (16)	0.235	0.353	−0.056
C(114)	0.2287 (4)	0.2676 (2)	0.0185 (2)	4.49 (16)	0.218	0.229	−0.019
C(115)	0.2330 (4)	0.2500 (2)	0.0918 (2)	4.33 (16)	0.227	0.199	0.107
C(116)	0.2477 (4)	0.3047 (2)	0.1435 (2)	3.29 (13)	0.252	0.293	0.196
C(121)	0.3617 (3)	0.4144 (2)	0.2601 (2)	2.79 (11)			
C(122)	0.4381 (4)	0.3611 (2)	0.2464 (2)	3.59 (13)	0.442	0.341	0.196
C(123)	0.5093 (4)	0.3368 (2)	0.3021 (3)	4.59 (16)	0.563	0.298	0.292
C(124)	0.5041 (4)	0.3657 (3)	0.3714 (2)	4.52 (16)	0.554	0.347	0.411
C(125)	0.4277 (4)	0.4190 (3)	0.3850 (2)	4.75 (17)	0.423	0.439	0.435
C(126)	0.3565 (3)	0.4434 (2)	0.3293 (2)	3.51 (13)	0.302	0.481	0.339
C(131)	0.3457 (3)	0.5204 (2)	0.1475 (2)	2.88 (12)			
C(132)	0.4464 (4)	0.5018 (2)	0.1227 (3)	4.46 (16)	0.475	0.451	0.129
C(133)	0.5087 (3)	0.5541 (3)	0.0897 (3)	4.80 (17)	0.581	0.540	0.072
C(134)	0.4702 (4)	0.6251 (2)	0.0816 (3)	4.43 (16)	0.515	0.662	0.058
C(135)	0.3696 (4)	0.6437 (2)	0.1064 (3)	4.03 (15)	0.343	0.694	0.100
C(136)	0.3073 (3)	0.5914 (2)	0.1394 (2)	3.64 (14)	0.236	0.605	0.157
C(211)	−0.1469 (3)	0.5143 (2)	0.3359 (2)	2.73 (11)			
C(212)	−0.2525 (3)	0.4969 (3)	0.3521 (2)	3.47 (13)	−0.304	0.478	0.314
C(213)	−0.2859 (3)	0.5063 (3)	0.4222 (2)	4.36 (15)	−0.361	0.494	0.434
C(214)	−0.2137 (4)	0.5331 (3)	0.4761 (2)	4.43 (16)	−0.237	0.540	0.526
C(215)	−0.1081 (3)	0.5505 (3)	0.4599 (2)	4.08 (15)	−0.055	0.569	0.498
C(216)	−0.0747 (3)	0.5411 (2)	0.3898 (2)	3.07 (12)	0.001	0.553	0.378
C(221)	−0.1895 (3)	0.4506 (2)	0.1931 (2)	2.69 (11)			
C(222)	−0.2178 (4)	0.3839 (2)	0.2227 (2)	3.90 (14)	−0.197	0.374	0.274
C(223)	−0.2766 (4)	0.3334 (2)	0.1805 (3)	5.09 (18)	−0.298	0.287	0.202
C(224)	−0.3070 (4)	0.3494 (3)	0.1087 (3)	5.14 (18)	−0.349	0.313	0.079
C(225)	−0.2787 (4)	0.4161 (3)	0.0792 (2)	5.07 (17)	−0.299	0.427	0.027
C(226)	−0.2200 (4)	0.4666 (2)	0.1214 (2)	3.82 (14)	−0.199	0.514	0.099
C(231)	−0.1471 (3)	0.6028 (2)	0.2133 (2)	2.66 (11)			
C(232)	−0.0746 (2)	0.6577 (2)	0.1972 (2)	3.23 (13)	0.005	0.647	0.198
C(233)	−0.1127 (3)	0.7270 (2)	0.1787 (2)	3.52 (13)	−0.060	0.766	0.167
C(234)	−0.2235 (3)	0.7412 (2)	0.1762 (2)	3.54 (14)	−0.250	0.791	0.163
C(235)	−0.2960 (3)	0.6863 (2)	0.1922 (2)	3.64 (14)	−0.375	0.697	0.190
C(236)	−0.2579 (3)	0.6171 (2)	0.2108 (2)	3.38 (13)	−0.310	0.578	0.222
H(171)				4.5	−0.098	0.150	−0.097
H(172)				4.5	−0.220	0.159	−0.071
H(173)				4.5	−0.169	0.221	−0.122

[a] C(*xx*1) is attached to P, and the atoms in the ring are sequentially numbered around the ring. [b] Isotropic thermal parameters of the phenyl hydrogen atoms are taken as the same as those of the respective carbon atoms to which they are bonded; the units are Å². [c] For $RuCl_3(NO)(PPh_3)_2$. [d] For $RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2 \cdot CH_2Cl_2$.

contains a less bulky ammine in place of a nitrosyl ligand, the phosphines bend *toward* the ammine by a small amount (0.3°). Furthermore, the chloro ligands which are trans to each other also bend toward the ammine as evidenced by the N–Os–Cl angle at 84.68 (5)°; the analogous angle in $RuCl_3(NO)(PPh_3)_2$ is 89.17 (4)°. To a smaller extent in $OsCl_3(NH_3)(PPh_3)_2$ when a less bulky ammine ligand is present and to a larger extent in $IrCl_2(NO)(PPh_3)_2$[36] and $ReCl_2N(PPh_3)_2$[30] when no ligand is present, the trans chloro ligands bend away from the chloro, nitrosyl, and nitrido ligands, respectively, in order to relieve the strain caused by rings 1 and 3 of the triphenylphosphine ligands. It is now clear why the five-coordinate

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

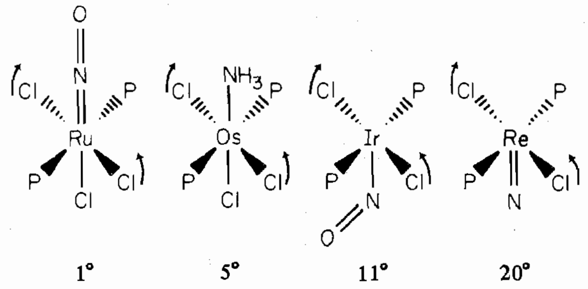
Atom	Min	Intermed	Max
Ru[a]	0.150 (1)	0.152 (1)	0.169 (1)
Cl(1)	0.178 (2)	0.208 (2)	0.228 (2)
Cl(2)	0.162 (3)	0.196 (3)	0.203 (3)
P	0.154 (2)	0.158 (2)	0.178 (2)
O	0.161 (12)	0.206 (9)	0.318 (10)
N	0.149 (11)	0.184 (10)	0.187 (11)
Ru[b]	0.144 (1)	0.163 (1)	0.177 (1)
Cl(1)	0.166 (2)	0.209 (2)	0.231 (2)
Cl(2)	0.170 (2)	0.196 (2)	0.223 (2)
Cl(3)	0.151 (3)	0.205 (2)	0.231 (2)
Cl(4)[c]	0.337 (6)	0.464 (7)	0.794 (10)
Cl(5)[c]	0.316 (5)	0.494 (7)	0.692 (9)
P(1)	0.166 (3)	0.177 (2)	0.186 (2)
P(2)	0.162 (3)	0.168 (3)	0.181 (2)
N(1)	0.152 (9)	0.178 (8)	0.190 (8)
N(2)	0.156 (10)	0.192 (8)	0.229 (8)
C(17)	0.166 (12)	0.279 (11)	0.301 (11)
C(1)[c]	0.290 (19)	0.462 (23)	0.577 (26)

[a] For $RuCl_3(NO)(PPh_3)_2$. [b] For $RuCl_3(p\text{-}NNC_6H_4CH_3)_2 \cdot CH_2Cl_2$. [c] These atoms belong to the solvent molecule, CH_2Cl_2.

Table V. Selected Distances (Å) and Angles (deg) in $RuCl_3(NO)(PPh_3)_2$

	Bond Distances		
Ru–Cl(1)	2.394 (2)	N–O	1.142 (8)
Ru–Cl(2)	2.353 (2)	P–C(11)	1.823 (4)
Ru–P	2.465 (1)	P–C(21)	1.824 (3)
Ru–N	1.737 (7)	P–C(31)	1.827 (4)
	Intramolecular Nonbonded Distances		
H(16)–Cl(1)	2.58	H(32)–Cl(2)	2.79
H(16)–Cl(2)	2.84	H(26)–H(36)	2.34
	Bond Angles[a]		
N–Ru–Cl(2)	180	Cl(1)′–Ru–P	86.90 (5)
Cl(1)–Ru–Cl(1)′	178.35 (9)	Cl(2)–Ru–P	88.75 (4)
P–Ru–P′	177.49 (8)	Ru–P–C(11)	119.1 (1)
Ru–N–O	180	Ru–P–C(21)	106.4 (1)
Cl(1)–Ru–N	89.17 (4)	Ru–P–C(31)	117.4 (1)
P–Ru–N	91.25 (4)	C(11)–P–C(21)	106.6 (2)
Cl(1)–Ru–Cl(2)	90.83 (4)	C(11)–P–C(31)	100.8 (2)
Cl(1)–Ru–P	93.13 (5)	C(21)–P–C(31)	105.3 (2)
	Dihedral Angles		
[Ru–P–C(11)]–[P–C(12)–C(11)]			2.4 (3)
[Ru–P–C(21)]–[P–C(21)–C(26)]			65.3 (3)
[Ru–P–C(31)]–[P–C(31)–C(32)]			64.2 (4)

[a] Cl(1)′ and P′ are related to Cl(1) and P by the C_2 axis.



nitrido and nitrosyl complexes are "upside down" with respect to the six-coordinate ammine and nitrosyl complexes; i.e., the metal–nitrogen vectors have opposite signs. The trans chloro ligands bend toward the least crowded site in order to relieve the steric strain caused by the bulky phosphine ligands. Thus, the triphenylphosphine and the nitrido or nitrosyl ligands work together in the same manner and cause the Cl–M–Cl angle in the five-coordinate Re and Ir complexes to become more acute.

Description of the Tolyldiazo Structure. The structure of $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2 \cdot CH_2Cl_2$ consists of discrete, well-separated monomers and solvent molecules. The labeling scheme for the complex, together with some bond distances and angles in the inner coordination sphere, is shown in Figures 1 and 4. A stereodrawing for the unit cell has been omitted because it is very similar to the one already published for the acetone solvate of the same complex.[24] The complex has pseudooctahedral geometry with trans phosphine ligands, meridional chloro ligands, and a singly bent *p*-tolyldiazo ligand. The three mutually perpendicular coordination planes are reasonably well defined. There are no significant intermolecular contacts, the shortest being H(123)–H(223) = 2.47 Å and H(125)–H(214) = 2.49 Å.

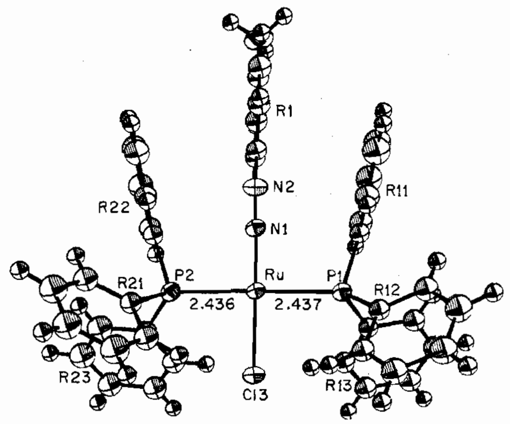


Figure 4. A molecule of $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2 \cdot CH_2Cl_2$ with Cl(1), Cl(2), and the solvent molecule missing. The phenyl rings are appropriately numbered. Vibrational ellipsoids are drawn at the 50% probability level except for the hydrogen atoms whose isotropic thermal parameters were reduced by one-half. The molecule has no imposed symmetry but has approximate C_s symmetry with Ru, Cl(1), Cl(2), Cl(3), N(1), N(2), and ring 1 lying near the approximate mirror plane.

A comparison of results of the two structural determinations (see Table VI) of the ruthenium tolyldiazo complex shows the structures to be virtually the same in their gross features despite the presence of different solvent molecules. Indeed, in both structures the solvent sits in a large cavity created by the inefficient packing of the molecules which is caused by the presence of the bulky tolyldiazo ligand. Comparison of all significant bond distances and angles shows the two complexes to be very similar. Table VII contains bond angles and distances for the tolyldiazo complex; certain corresponding values for the previously determined structure appear in brackets. It is gratifying that two different structure determinations performed on different crystals in different laboratories yield such similar results. This suggests that our present methods for estimating errors are reliable. We find only a few differences between the structures. The Cl(3)–Ru–P(1) and Cl(1)–Ru–Cl(2) angles are slightly different; whereas the two independent Ru–P distances were slightly unequal (difference 0.009 Å) in the previous structure, they are equal in our structure. There are other small differences in the structures, but their significance cannot be evaluated because different models were chosen; McArdle et al.[24] refined the tolyl group as seven individual isotropic atoms while we refined the C_6 group as a rigid body and the para methyl carbon as an anisotropic atom. McArdle et al. terminated data collection at $2\theta = 45°$, whereas our data set extended to 47.5°. Moreover, whereas McArdle et al. used the 2478 data having $F_o^2 > 3.7\sigma(F_o^2)$, we used 5100 data having $F_o^2 > 3.0\sigma(F_o^2)$. (Compared with the 2478 reflections used by McArdle et al., we have in our data set 4210 obeying the exact same conditions; obviously the signal-to-noise ratio was better in our experiment, presumably because a larger crystal was used.) The increased number of data used in the present experiment results in noticeably improved standard deviations in distances and angles. The fact that our data extend to higher angles

Table VI. Comparison of Structural Data for Six-Coordinate Ru and Os Complexes, $MCl_3(L)(PPh_2R)_2$

Distance or angle[a]	M = Ru, R = Ph, L = $N_2C_6H_4Me$,[b] Me_2CO solvate	M = Ru, R = Ph, L = $N_2C_6H_4Me$,[c] CH_2Cl_2 solvate	M = Ru, R = Ph, L = NO,[d] no solvent	M = Ru, R = Me, L = NO,[e] no solvent	M = Os, R = Ph, L = NH_3,[f] no solvent
M-N(1)	1.796 (9)	1.784 (5)	1.737 (7)	1.744 (6)	2.136 (9)
N(1)-X[h]	1.144 (10)	1.158 (6)	1.142 (8)	1.132 (6)	
N(2)-C(11)	1.40 (1)	1.376 (6)			
M-Cl, trans to N	2.385 (3)	2.382 (2)	2.353 (2)	2.357 (2)	2.360 (3)
M-Cl, trans to Cl[i]	2.390 (5)	2.390 (3)	2.394 (2)	2.398 (10)	2.363 (2)
M-P[i]	2.434 (6)	2.437 (2)	2.465 (1)	2.435 (8)	2.411 (2)
M-N(1)-X[h]	171.2 (9)	171.9 (5)	180.0[g]	176.4 (6)	
N(1)-N(2)-C(11)	135.9 (11)	137.1 (5)			
N(2)-C(11)-C(16)	121 (1)	121.6 (4)			
N(1)-M-P[i]	90.4 (4)	90.6 (2)	91.25 (4)	94.1 (8)	89.69 (5)
N(1)-M-Cl[i]	89.0 (10)	88.8 (10)	89.17 (4)	90 (3)	84.68 (5)

[a] Distances given in angstroms and angles given in degrees. Abbreviations: Ph, C_6H_5; Me, CH_3; R, organic group. For averaged quantities, the error is the larger of (1) an individual standard deviation or (2) the standard deviation of a single observation as calculated from the mean. [b] See ref 24. [c] This work; this molecule has no imposed symmetry but has approximate C_s symmetry. [d] This work; this molecule has imposed C_2 symmetry. [e] See ref 25. [f] See ref 35; this molecule has imposed C_2 symmetry. [g] Linear angle required by symmetry. [h] X = N(2) or O. [i] Average value.

may also be responsible for another apparent difference between the two structures: relative to our results, the atom N(1) is shifted in the previous structure determination away from Ru toward N(2) by about 0.013 Å, thus lengthening the Ru-N(1) distance and shortening the N(1)-N(2) distance. One would expect the greatest effect of a more limited data set to be on a highly polar bond between light atoms.[42,43]

As in the nitrosyl structure, the metal-ligand distances fall in the expected ranges. The Ru-P distances at 2.436 (2) and 2.437 (2) Å, the Ru-N(1) distance at 1.784(5) Å, and the Ru-Cl(trans to Cl) distances, 2.387 (2) and 2.392 (2) Å, are all normal (see discussion of the nitrosyl complex). The Ru-Cl (trans to N) distance at 2.382 (2) Å is not shortened to the extent that is found in the nitrosyl complex.

The tolyldiazo complex is even more crowded than its nitrosyl analogue, and its intramolecular geometry is primarily governed by the nonbonded interactions of the tolyldiazo group with the two bulky triphenylphosphine ligands. The molecule has no imposed symmetry, but there is an approximate mirror plane relating the two similar phosphine ligands which have significantly different conformations than those in the analogous nitrosyl complex. Rings 13 and 23 in the diazo complex are oriented in a manner similar to ring 1' in the nitrosyl complex, and they are wedged between Cl(3) and Cl(1) causing Cl(3) to move away from Cl(1) and toward Cl(2). As is evident from Figure 4, rings 11 and 22, corresponding to rings 2 and 2' in the nitrosyl complex, are sharply twisted about their P-C bonds in order to accommodate the tolyldiazo group so that the three aryl groups are as parallel as they can be; the large torsion angles about P(2)-C(221) and P(1)-C(111) result from this interaction. Owing to ortho hydrogen contacts with rings 22 and 11, rings 21 and 12 cannot adopt the conformation of ring 3 in the nitrosyl complex; they rotate about their P-C bonds and orient themselves as rings 23 and 13 but between atoms Cl(2) and Cl(3). The shortest, nonbonded, intramolecular contacts result from the crowding of these two rings (12 and 21): H(122)-H(116) = 2.51, H(122)-H(132) = 2.43, H(212)-H(222) = 2.47, and H(212)-H(236) = 2.50 Å. Thus, the triphenylphosphine ligands in the tolyldiazo complex have an unusual "mirror conformation" in which rings 11 and 22 are located on the "mirror" and straddle it.

The dichloromethane solvent, which sits in a cavity in the tolyldiazo structure, is not well-behaved as evidenced by the excessive thermal motion, by the nonrepresentative geometry (C-Cl = 1.39 and 1.68 Å, Cl-C-Cl = 122°), and by the fact that the hydrogen atoms of the solvent could not be located.

Nitrosyl and Phenyldiazo Ligands. As already noted the nitrosyl ligand is linear and the tolyldiazo ligand is singly bent indicating sp hybridization about the coordinated nitrogen atom in both ligands. The linear mode of coordination for nitrosyl ligands is commonly observed, and the singly bent geometry for aryldiazo ligands has also been observed in Mo,[19] Re,[26] and Fe[27] complexes. The N-N-C(phenyl) angles in these last three complexes fall in the range 119-125° and are indicative of sp^2 hybridization about the uncoordinated nitrogen atom. This also suggests that the hybridization about the oxygen atom in the nitrosyl complex is sp^2. This is in accord with the frequently written valence-bond description of linear nitrosyl complexes analogous to geometry A. However, the corresponding angle in the Ru complex is distinctly larger, 137.1 (5)°. A comparison of the four known singly bent aryldiazo structures suggests that the Ru complex represents an intermediate geometry between A and C, singly bent and totally linear, albeit closer to A.[27] If this is true, the Ru-N(1) distance and N(1)-N(2)-C(11) angle should increase, and the N(1)-N(2) distance should decrease. The NNC angle is the largest yet observed and the N-N distance is the shortest yet observed, but the Ru-N distance, although longer by 0.047 (8) Å than in the nitrosyl complex, is still relatively short. We thus describe the tolyldiazo geometry as being singly bent with distinct distortions toward the totally linear geometry. In accordance with our earlier suggestions and with those of McArdle et al.[24] and Laing et al.,[13] we consider linear nitrosyl ligands and singly bent aryldiazo ligands to be coordinated to a metal as NO^+ and $NNAr^+$ in a formal sense, and we consider the complexes to contain Ru(II). Some other authors have formally described singly bent diazo ligands as though they were uninegative.[26]

The question arises as to whether the distortions away from expected singly bent geometry observed in the ruthenium-tolyldiazo complex are a result of steric forces in the molecule or a result of the electronic interaction of ligand and metal. Indeed, the complex is crowded, and there are obvious steric influences resulting from the interactions of the diazo and phosphine ligands, as already noted. Such interactions would probably result in the tolyl group being pushed away from the metal with a concomitant lengthening of bonds, opening of the N-N-C angle, and bending of the Ru-N-N angle. No appreciable bond lengthening is observed; on the contrary, the N-N bond shortens, but the expected distortion of angles is observed. Although we cannot estimate quantitatively the relative magnitudes of the steric and electronic influences, we feel that the large distortions in the diazo ligand away from expected singly bent geometry are too large to be caused by steric influences alone and that to a significant degree the structural results are indicative of the metal-aryldiazo ligand electronic interaction.

Table VII. Selected Distances (Å) and Angles (deg) in $RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2 \cdot CH_2Cl_2$

	Bond Distances		
Ru–Cl(1)	2.392 (2)	P(2)–C(231)	1.832 (4)
Ru–Cl(3)	2.382 (2)	P(2)–C(211)	1.826 (4)
Ru–Cl(2)	2.387 (2)	P(2)–C(221)	1.819 (4)
Ru–P(2)	2.436 (2) [2.429 (4)][a]	P(1)–C(131)	1.848 (4)
Ru–P(1)	2.437 (2)	P(1)–C(121)	1.831 (4)
Ru–N(1)	1.784 (5) [1.796 (9)][a]	P(1)–C(111)	1.822 (4)
N(1)–N(2)	1.158 (6) [1.144 (10)][a]	C(1)–Cl(4)	1.39 (2)
N(2)–C(11)	1.376 (6) [1.40 (1)][a]	C(1)–Cl(5)	1.68 (2)
C(14)–C(17)	1.506 (9) [1.54 (2)][a]		
	Intramolecular Nonbonded Distances		
N(1)–H(16)	2.80	N(1)–P(1)	3.034 (5)
Cl(3)–H(136)	2.60	Cl(1)–Cl(3)	3.512 (3)
Cl(3)–H(232)	2.60	Cl(1)–P(1)	3.304 (3)
H(116)–H(122)	2.51	Cl(2)–Cl(3)	3.305 (3)
H(212)–H(236)	2.50	Cl(3)–P(2)	3.435 (3)
H(122)–H(132)	2.43	Cl(3)–P(1)	3.363 (3)
H(212)–H(222)	2.47	Cl(2)–P(2)	3.425 (3)
N(1)–Cl(1)	2.970 (5)	Cl(2)–P(1)	3.583 (3)
N(1)–Cl(2)	2.933 (5)	Cl(1)–P(2)	3.333 (2)
N(1)–P(2)	3.031 (5)		
	Bond Angles		
Ru–N(1)–N(2)	171.9 (5)	N(2)–C(11)–C(16)	121.6 (4)
N(1)–N(2)–C(11)	137.1 (5) [135.9 (11)][a]	N(2)–C(11)–C(12)	118.4 (3) [117 (1)][a]
N(1)–Ru–Cl(3)	175.6 (2)	C(15)–C(14)–C(17)	119.7 (4)
Cl(1)–Ru–Cl(2)	176.74 (6) [177.1 (1)][a]	C(13)–C(14)–C(17)	120.3 (4) [122 (1)][a]
P(1)–Ru–P(2)	173.56 (6)	Cl(4)–C(1)–Cl(5)	122 (1)
N(1)–Ru–Cl(1)	89.5 (2)	Ru–P(1)–C(111)	108.1 (2)
N(1)–Ru–Cl(2)	88.1 (2)	Ru–P(1)–C(121)	117.9 (1)
N(1)–Ru–P(2)	90.5 (2)	Ru–P(1)–C(131)	118.8 (1)
N(1)–Ru–P(1)	90.6 (2)	C(111)–P(1)–C(121)	104.6 (2)
Cl(1)–Ru–Cl(3)	94.71 (7)	C(111)–P(1)–C(131)	103.8 (2)
Cl(1)–Ru–P(1)	86.34 (6)	C(121)–P(1)–C(131)	102.0 (2)
Cl(2)–Ru–Cl(3)	87.74 (7) [87.5 (1)][a]	Ru–P(2)–C(211)	119.7 (1)
Cl(3)–Ru–P(2)	90.94 (6)	Ru–P(2)–C(221)	106.7 (2)
Cl(3)–Ru–P(1)	88.50 (6) [89.0 (1)][a]	Ru–P(2)–C(231)	118.5 (1)
Cl(2)–Ru–P(2)	90.49 (6)	C(211)–P(2)–C(221)	106.6 (2)
Cl(3)–Ru–P(1)	88.50 (6) [89.0 (1)][a]	C(211)–P(2)–C(231)	99.9 (2)
Cl(2)–Ru–P(2)	90.49 (6)	C(221)–P(2)–C(231)	103.8 (2)
Cl(2)–Ru–P(1)	95.89 (6)		
Cl(1)–Ru–P(2)	87.32 (6)		
	Dihedral Angles		
[Ru–N(2)–N(1)]–[Cl(1)–Ru–N(1)]	2.2 (3.5)		
[Ru–N(1)–N(2)]–[Cl(2)–Ru–N(1)]	0.0 (3.4)		
[N(1)–N(2)–Ru]–[N(2)–N(1)–C(11)]	1.7 (2.9)		
[N(1)–N(2)–C(11)]–[N(2)–C(11)–C(16)]	2.8 (1.0)		
[P(1)–C(111)–Ru]–[C(116)–P(1)–C(111)]	81.2 (4)		
[P(1)–C(121)–Ru]–[C(126)–P(1)–C(121)]	37.3 (4)		
[Ru–P(1)–C(131)]–[P(1)–C(131)–C(136)]	5.0 (4)		
[Ru–P(2)–C(211)]–[P(2)–C(211)–C(216)]	40.9 (4)		
[Ru–P(2)–C(221)]–[P(2)–C(221)–C(222)]	85.4 (4)		
[P(2)–C(231)–Ru]–[C(232)–P(2)–C(231)]	18.4 (4)		

[a] Corresponding value for $RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2 \cdot C_3H_6O$; see ref 24.

In light of the small bending (5–8°) of the NO and NNAr ligands in $RuCl_3(NO)(PPh_2Me)_2$ and $RuCl_3(NNAr)(PPh_3)_2$ and the disorder in $IrCl_2(NO)(PPh_3)_2$, the possibility of slight disorder of the oxygen atom of the nitrosyl in $RuCl_3(NO)(PPh_3)_2$ was considered. There was no indication of a "peanut shape" in electron density maps. The maximum electron density was exactly on the C_2 axis. Although the thermal ellipsoid is somewhat elongated normal to the NO bond, such motion is typical of oxygen atoms in carbonyl and nitrosyl complexes. A comparison of the thermal motion of the oxygen atom with those in $RuCl_3(NO)(PPh_2Me)_2$ and $Ru(NO)_2(PPh_3)_2$[44] reveals nothing unusual about the orientation or magnitude of the motion. If there is slight disorder, we cannot detect it crystallographically. We feel that the symmetric environment of the oxygen atom causes the Ru–N–O angle to maintain complete linearity.

A comparison of the metric parameters of the nitrosyl and tolyldiazo ligands in the same complex shows that both ligands are good π acceptors but that the nitrosyl ligand is the better of the two. Convincing evidence for this fact comes from the shortening of the metal–chlorine distance which is trans to the nitrogen ligand. The respective differences in distances are 0.041 (3), 0.008 (3), and 0.003 (4) Å in $RuCl_3(NO)(PPh_3)_2$, $RuCl_3(NNAr)(PPh_3)_2$, and $OsCl_3(NH_3)(PPh_3)_2$. There is a distinct shortening in the nitrosyl complex but only a slight shortening in the tolyldiazo complex. Notwithstanding, the short Ru–N distance in the diazo complex indicates the presence of a significant π interaction. The shortening of the metal–ligand bond trans to a linear nitrosyl ligand has been observed before.[5,45] This observation is consistent with the reaction chemistry of some of these complexes. Complexes of the type $MX_3(NO)P_2$ (M = Os, Ru; P = mono(tertiary phosphine); X = Cl, NO_2) can undergo a halide displacement

$$RuCl_3(NO)P_2 \xrightarrow{-Cl^-} \text{“}RuCl_2(NO)P_2{}^{+}\text{”} \xrightarrow{+P} RuCl_2(NO)P_3{}^{+}$$

$$ReCl_3(NO)P_2{}^{-} \xrightarrow{-Cl^-} ReCl_2(NO)P_2 \xrightarrow{+P} ReCl_2(NO)P_3$$

reaction in the presence of excess phosphine.[46,47] The final cationic tris(phosphine) complex contains meridional phosphine ligands and cis chloro ligands indicating that the trans ON–Ru–Cl unit remained intact during the reaction. Although the five-coordinate intermediate was not isolated, we presume that it is square pyramidal (d^6, Ru(II)) with an almost linear ON–Ru–Cl unit in the basal plane because removing a chloro ligand trans to another chloro ligand should be easier than removing one which is trans to a nitrosyl ligand. It is interesting that all three of the isoelectronic rhenium complexes are known although they were not necessarily prepared according to the previous sequence.[48] The stereochemistry of the tris(phosphine) complex is the same as that of the cationic ruthenium analogue. It is reasonable to expect that both rhenium bis(phosphine) complexes have the same stereochemistry as the analogous ruthenium complexes.

There are other observations which point, though not unambiguously, to the greater π-accepting ability of the nitrosyl ligand. (1) The metal–nitrogen distance is shorter by 0.047 (8) Å. This shortening in the nitrosyl complex, however, could result from better σ-bonding characteristics. (2) The N–O distance should be 0.03 Å shorter than a corresponding N–N distance;[49] yet it is only 0.014 (10) Å shorter. However, the differences are at best marginally significant especially in light of the possible systematic error in the N–O distance caused by thermal motion. (3) Even with the smaller nitrosyl ligand present, the N–Ru–P angles are larger in the nitrosyl complex. Although McArdle et al.[25] used this observation as a measure of the extent of π bonding in the cis nitrosyl ligand, we feel that the differences in these angles are also strongly influenced by the conformations of the triphenylphosphine ligands which are very different in the nitrosyl and tolyldiazo structures; hence it is difficult to interpret these differences in angles.

N–O and N–N Stretching Frequencies.[50] Since the values of N–O stretching frequencies in nitrosyl complexes span a 500-cm^{-1} range, it was thought that ν(NO) would be diagnostic of the mode of coordination of the NO ligand; lower values were considered to be indicative of bent nitrosyl ligands and higher values were considered to be indicative of linear nitrosyl ligands. This method was shown to be less reliable

Chart I

Metal		Group		Charge		Ligands	
First row	−50	6B	+100	2+	−140	Third PR_3	+20
Second row	−30	7B	+50	1+	−80	Fourth PR_3	+50
(Mo, −10)		8	0	Neutral	0	$HB(pz)_3^-$	−20
Third row	0			1−	+80	$C_5H_4PPh_3$	+60
				2−	+140	H^-	+20
				3−	+200		

Coordination number: four, +50; five-six-seven, 0

because of a large region of overlap in which both linear and bent nitrosyl ligands could be found. It is clear that certain electronic factors cause distinct changes in the value of ν(NO) without changing the basic coordination geometry. Thus, after examining several hundred nitrosyl complexes which were reported in the literature and with the aid of the structural work involving nitrosyl complexes, we developed a set of empirical rules which attempts to correct for these factors in even-electron complexes. A brief report of the rules has appeared earlier.[20]

In order to understand more clearly the effect of a dipositive charge on the N–O stretching frequency in a cationic complex, we prepared the complexes $[M(NO)(diphos)_2]^{2+}$ (M = Rh, Ir) for comparison with $Ru(NO)(diphos)_2^+$ and $Co(NO)(diars)_2^{2+}$. We also prepared the ^{15}N-substituted rhodium nitrosyl complex; its N–O stretching frequency shifted the calculated amount, 31 cm^{-1}. While this work was in progress, the preparation of the Rh complex was reported by two other groups of workers.[51,52] The green Rh complex undergoes a reversible reaction with excess halide ion to form an orange-yellow product which we presume to be the six-coordinate complex, but we have not yet been able to isolate the product in a pure state.

$$[M(diphos)_2][PF_6] + [NO][PF_6] \rightarrow [M(NO)(diphos)_2][PF_6]_2 \quad (M = Rh, Ir)$$

The corrections shown in Chart I are either added to or subtracted from the observed N–O stretching frequency (cm^{-1}). When these 15 corrections are applied to large numbers of nitrosyl complexes, one finds that the corrected stretching frequencies, ν', fall into at least two groups, those above and below 1610–1620 cm^{-1}. Bent nitrosyl ligands fall in the lower range and linear nitrosyl ligands fall into the higher range. Several interesting trends are observable when similar complexes are classified on the basis of the values of ν'. All 16-electron systems, regardless of coordination number, have high values of ν' [ν; ν']: $IrCl(NO)(PPh_3)_2^+$ [1890; 1860], $ReCl_2(NO)(PPh_3)_2$[48] [1725; 1775], $ReCl(CO)(NO)(PPh_3)_2^+$ [1810; 1780],[11] $Mn(NO)(S_2C_2(CN)_2)_2^{2-}$ [1687; 1827], $Fe(NO)(S_2C_2(CN)_2)_2^-$ [1857; 1887], $MoCl_3(NO)(OPPh_3)_2$ [1710; 1800], $WCl_3(NO)(OPPh_3)_2$ [1650; 1750]. Similarly, all 18-electron, six-coordinate complexes have high values of ν' even though the measured values of ν(NO) are sometimes low: $CpMo(NO)(PPh_3)_2$ [1561; 1651], $(HB(pz)_3)W(NO)I_2(PPh_3)$[53] [1610; 1730], CpCr(NO)(CO)(PPh_3) [1654; 1704], CpMo(NO)(CO)(PPh_3) [1617; 1707], CpW(NO)(CO)(PPh_3) [1605; 1750], $ReCl_3(NO)(PPh_2Me)_2^-$ [1670; 1800],[48] $OsCl_3(NO)(PPh_3)_2$ [1850; 1850], $IrCl_3(NO)(PPh_3)_2^+$ [1945; 1865], $RuCl_3(NO)(PPh_3)_2$ [1876; 1846], $CrCl(NO)(diars)_2$ [1590; 1710], $FeCl(NO)(diars)_2^{2+}$ [1883; 1763].[54] All 20-electron complexes in which the integrity of the nitrosyl ligand remains intact should have bent nitrosyl ligands and low values of ν': $CoCl(NO)(en)_2^+$ [1611; 1481], $Co(OClO_3)(NO)(en)_2^+$ [1663; 1533], $CoCl(NO)(diars)_2^+$ [1562; 1432], $Co(NO)(NH_3)_5^{2+}$ [1620; 1430], $Rh(NO)(dtc)_3^+$ [1545; 1435].[51] At first glance, $Cp_3Mo(NO)$ [1610; 1700], $Cp_2Mo(NO)I$ [1647; 1738], and $Ru(NO)(dtc)_3$ [1803; 1773] appear to be exceptions. Compare this Ru complex with $Mo(NO)(dtc)_3$ [1640; 1730]. However, the cyclopentadienyl ligands are not all η^5 and one of the dithiocarbamate ligands in the Ru complex is not bidentate; thus, the linear nitrosyl ligands anticipated on the basis of ν' are compatible with an 18-electron count for each complex.

We are not sure that ν' can be used to distinguish bridging and nonbridging nitrosyl ligands; however, preliminary observations are encouraging. The compounds $(HB(pz)_3)_2W_2(NO)_2I_4$ [1645; 1725],[53] $Cp_2Mo_2(NO)_2I_4$ [1670; 1760], and $CpMo_2(NO)_2I_2$ [1573; 1663] should contain only terminal linear nitrosyl ligands. $Cp_2Fe_2(NO)_2Me_2$ [1572, 1504; 1522, 1454] and $Cp_2Co_2(NO)_2$ [1585, 1525; 1535, 1475] should contain only bridging ligands. Finally, $Cp_2Mn_2(CO)_2(NO)_2$ [1709, 1509; 1709, 1509] and $Cp_2Cr_2(NO)_4$ [1670, 1505; 1720, 1555] should contain bridging and terminal nitrosyl ligands.

Although the possibility of both tetrahedral and square-planar geometries exists for four-coordinate, 18-electron nitrosyl complexes, only pseudotetrahedral complexes with linear nitrosyl ligands have been characterized structurally. A survey of many such complexes reveals the presence of only linear nitrosyl ligands based on the values of ν', e.g., $Co(NO)(CN)^{3-}$ [1485; 1685], $Co(NO)_2(PPh_3)_2^+$ [1855, 1795; 1775, 1715],[55] $Pt(CF_3)(NO)(PPh_3)_2$ [1660; 1710], and $NiBr(NO)(PPh_3)_2$ [1735; 1735].[56]

When these empirical rules are applied to five-coordinate, 18-electron nitrosyl complexes, the correct ligand geometry is predicted in every case in which the result may be tested with *only one exception*, $IrI(CO)(NO)(PPh_3)_2^+$ [1720, 1640]. Only two complexes fall in the borderline region, and they would not be borderline cases if we more rigidly defined the borderline as 1606–1611 cm^{-1}: $Ir(NO)(C_2F_4)(PPh_3)_3$ [1600; 1620], $RuI(CO)(NO)(PPh_3)_2$ [1642; 1612]. No effort will be made to document observed and corrected N–O stretching frequencies in these five-coordinate complexes; the reader is referred to several review articles from which the desired information can be obtained.[1-4] Several interesting results did emerge, however, from our survey of five-coordinate complexes. $Rh(NO)(diphos)_2^{2+}$ [1748; 1648] and $RhCl(NO)(PPh_3)_3^+$ [1720; 1630] should have a linear nitrosyl ligands while certain related Rh complexes should have bent nitrosyl ligands, $Rh(NO)(MeCN)_2(PPh_3)_2^{2+}$ [1735; 1565],[51] $Rh(NO)(MeCN)_4^{2+}$ [1760; 1590],[51] $RhCl(NO)(ppp)^+$ [1695; 1605],[22] $Rh(NO)(BuNC)_4^{2+}$ [1765; 1595], $RhCl(NO)(MeCN)(PPh_3)_2^+$ [1705; 1595],[51] $RhCl(NO)(MeCN)_3^+$ [1700; 1590],[51] and $RhCl_2(NO)(PPh_3)_2$ [1630; 1600]. $OsCl(CO)(NO)(PPh_3)_2$ [1565; 1565] and $Os(OH)(NO)(NO)(PPh_3)_2^+$ [1842, 1632; 1762, 1552] should each contain one bent nitrosyl ligand while seemingly similar complexes probably contain only linear nitrosyl ligands, $OsH(CO)(NO)(PPh_3)_2$ [1630; 1650], $ReCl(NO)_2(PPh_3)_2$ [1650, 1600; 1700, 1650],[11] and $ReH(NO)_2(PPh_3)_2$ [1620, 1580; 1690, 1650].

We believe that these empirical rules are very useful in determining the mode of bonding of the nitrosyl ligand based only on the knowledge of the observed and corrected N–O stretching frequencies. Although modifications or additions may be necessary as new experimental information is available, their current utility is apparent. Although insufficient experimental information is presently available to warrant a firm conclusion, additional corrections may be necessary when methyl and nitro groups are present. We find that the values of ν' vary much more than expected for $IrCl_2(NO)(PPh_3)_2$ [1560; 1560], $IrCl(CH_3)(NO)(PPh_3)_2$ [1525; 1525],[58] and $IrCl(NO_2)(NO)(PPh_3)_2$ [1600; 1600].[59] Indeed, the crystal structures of $Ir(NO_2)_2(NO)(PPh_3)_2$ [1630; 1630][59] and of $Ir(CH_3)(CO)(NO)(PPh_3)_2^+$ [1680; 1600][59] would be valuable pieces of information in this regard.

The application of these empirical rules to aryldiazo complexes also yields good results. In this regard, they have special utility since fewer aryldiazo structures are known. There is really only one drawback: the values of ν(NN) are somewhat more difficult to determine (1) because they are 50–100 cm^{-1} lower than the corresponding values of ν(NO) in analogous nitrosyl complexes and are often hidden by vibrational modes of other ligands in the complex and (2) because the N–N stretching vibration is often vibrationally coupled with aryl vibrational modes. However, we have recently shown[5] that these difficulties can be easily and quickly overcome by mathematically decoupling the interacting bands which shift upon ^{2}H or ^{15}N substitution.

The only complexes with singly bent aryldiazo ligands whose structures are known with reasonable certainty are $RuCl_3(NNPh)(PPh_3)_2$ [1882; 1852],[13,60] $(HB(pz)_3)Mo(CO)_2(NNPh)$ [ca. 1590; ca. 1660],[61] $Fe(CO)_2(NNPh)(PPh_3)_2^+$ [1723; 1593],[62] and $ReCl_2(NH_3)(NNPh)(PPhMe_2)$ [ca. 1534; ca. 1584].[26,63] The only complexes with doubly bent aryldiazo ligands whose structures are known are $RhCl(NNPh)(ppp)^+$ [1603; 1513][5] and $PtCl(NNPh)(PEt_3)_2$[40] [1461; 1511].[40] The importance of using the corrected frequencies is manifest here; the uncorrected value of ν(NN) for the Rh complex is higher than those for the Mo and Re complexes, yet the values of ν' fall in the expected regions.

Since complexes with very large or very small values of ν' have either singly bent or doubly bent aryldiazo ligands, respectively, we need only concern ourselves with complexes whose values of ν' are in the intermediate region, 1500–1600 cm^{-1}. There are many aryldiazo complexes of Cr, Mo, and W, and all of them have ν' greater than 1590 cm^{-1} with singly bent aryldiazo ligands except one compound, $(HB(pz)_3)WI_4(NNPh)_2$[53] [ca. 1435; ca. 1515],[53] which probably contains a bridging diazo ligand.

On the basis of the current structural results and of other chemical considerations we believe that the corrected N–N stretching frequencies fall into at least two groups, those above and below 1530–1550 cm^{-1}. On this basis, $RhCl_2(NNPh)(PPh_3)_2$ [1577; 1547][5] is a borderline case, and the following complexes are expected to have singly bent ligand geometries: $RhCl(NNPh)(PPh_2Me)_3^+$ [ca. 1653; ca. 1563],[20] $IrCl(NNPh)(PPh_2Me)_3^+$ [1619; 1559],[64] $Ru(CO)_2(NNPh)(PPh_3)_2^+$ [1666; 1556],[20,64] $Os(CO)_2(NNPh)(PPh_3)_2^+$ [1661; 1581],[64] and $OsH(CO)(NNPh)(PPh_3)_2$ [1543; 1563].[5] The only possible exceptions are $Pt(NH_3)(p\text{-}FC_6H_4NN)(PEt_3)_2^+$ [ca. 1574; ca. 1544][65] and $Pt(p\text{-}FC_6H_4NN)(PEt_3)_3^+$ [ca. 1580; ca. 1570][65] which are claimed to be square planar with doubly bent aryldiazo ligands. Although neither Pt structure has been determined nor have the observed N–N stretching frequencies been verified by isotopic substitution, we subjectively tend to agree with the structural assignment, at least for the ammine–bis(phosphine) complex, but we feel the true uncoupled values of ν(NN) are probably lower. To date, no complexes have been prepared which have values of ν' in the 1515–1540-cm^{-1} region.

We believe that these empirical rules will be useful in understanding the behavior of nitrosyl complexes. Furthermore, since the development of the coordination chemistry of aryldiazo ligands is relatively recent, the structural considerations herein discussed should aid in understanding and developing new synthetic and reaction pathways.

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Registry No. $RuCl_3(NO)(PPh_3)_2$, 29826-79-7; $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2\cdot CH_2Cl_2$, 56817-34-6; $[Rh(NO)(diphos)_2][PF_6]_2$, 53738-67-3; $[Ir(NO)(diphos)_2][PF_6]_2$, 56817-36-8; $RuCl_2(PPh_3)_3$, 15529-49-4; *t*-BuONO, 540-80-7; $[Ir(diphos)_2][PF_6]$, 41047-09-0; $[Rh(diphos)_2][PF_6]$, 17374-65-1.

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 AIC502218-12-75.

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Crystal and Molecular Structure of Dinitrosylbis(triphenylphosphine)rhodium Perchlorate, $[Rh(NO)_2(P(C_6H_5)_3)_2][ClO_4]$

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The structure of dinitrosylbis(triphenylphosphine)rhodium perchlorate, $[Rh(NO)_2(P(C_6H_5)_3)_2][ClO_4]$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group $C2/c$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 17.134$ (4) Å, $b = 12.327$ (3) Å, $c = 17.166$ (4) Å, and $\beta = 108.17$ (2)°. The observed and calculated densities are 1.55 (3) and 1.52 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a value of the conventional R index (on F) of 0.061 for the 4649 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The crystal structure consists of well-separated, discrete, monomeric ions. The coordination geometry around the rhodium atom is best described as intermediate between tetrahedral and square planar; N–Rh–N = 157.5 (3) and P–Rh–P = 115.88 (5)°. The Rh–N–O angle is 158.9 (4)°. The dihedral angle between the N–Rh–N and P–Rh–P planes is 86.0 (1)°. The structure is compared with those of other isoelectronic $M(NO)_2(PPh_3)_2$ complexes, and trends in structure and activity as catalysts for the reaction $2NO + CO \rightarrow N_2O + CO_2$ are correlated.

Introduction

Complexes of the form $M(NO)_2P_2$, in which M is Fe, Ru, Os, Co^+, Rh^+, or Ir^+ and P is a phosphine, are of both structural and catalytic interest. Details of the geometrical structures may provide information about the electronic structures of the complexes and the ability of NO to act as a Lewis acid (NO^-) or a Lewis base (NO^+) on coordination. Several structures of $M(NO)_2(PPh_3)_2(Ph{=}C_6H_5)$ complexes have been determined: M = Fe,[1] Ru,[2,3] Os,[4] Co^+,[5] and Ir^+.[6] Certain of these complexes have been found to be catalysts for the reaction[7-10,11]

$$2NO + CO \rightarrow CO_2 + N_2O \qquad (1)$$

As the structure may reflect the electronic requirements of the metal center, we sought to determine the structure of $[Rh(NO)_2(PPh_3)_2][ClO_4]$ to complete the series of isoelectronic complexes and therefore to determine whether correlations could be made between structure and catalytic activity.

Experimental Section

The title compound was prepared from $Rh(NO)(PPh_3)_3$.[12] A sample of 2.15 g of $Rh(NO)(PPh_3)_3$ was dissolved in 100 ml of argon-saturated benzene. To 10 ml of cold methanol, 0.30 ml of *tert*-butyl nitrite and 0.25 ml of 70% $HClO_4$ were added. This solution was immediately added rapidly dropwise to the well-stirred $Rh(NO)(PPh_3)_3$ solution. The resulting solution was cooled to −20° overnight. The tiny black crystals were washed with ethanol; yield 76%; ν(NO) 1759, 1714 cm^{-1} (Nujol mull). Anal. Calcd for $C_{36}H_{30}ClN_2O_6P_2Rh$: C, 54.9; H, 3.9; N, 3.6. Found: C, 54.7; H, 3.5; N, 3.4.

Suitable crystals were grown by slowly diffusing ethanol into a concentrated solution of the complex in dichloromethane. A fragment with approximate dimensions 0.30 × 0.30 × 0.57 mm was cut from one of the deep purple needles. On the basis of optical goniometry, the principal faces were identified as belonging to the forms $\{\bar{1}11\}$ and $\{101\}$. One end of the crystal was jagged and was approximated by the faces (011), (110), and (100). On the basis of Weissenberg and precession photography using Cu Kα radiation, it was established that the crystal belongs to the monoclinic system. The observed extinctions $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ suggested the space groups $C2/c$ or Cc. By analogy to $[Ir(NO)_2(PPh_3)_2][ClO_4]$,[6] the space group was assumed to be $C2/c$. The lattice constants at 23°, which were determined from a least-squares refinement of the setting angles of 16 strong reflections which had been centered on a Picker FACS-1 diffractometer using Mo Kα radiation (λ 0.709300 Å), are $a = 17.134$ (4) Å, $b = 12.327$ (3) Å, $c = 17.166$ (4) Å, and $\beta = 108.17$ (2)°. The density calculated for four formula weights per unit cell is 1.52 g cm^{-3} which agrees well with the value of 1.55 (3) g cm^{-3} measured by suspending the crystals in a mixture of bromoform and ethanol. With four formula weights per unit cell either a twofold axis or a center of symmetry is imposed on the ions in $C2/c$.

For data collection Mo Kα radiation was used. The intensities were measured by the θ–2θ technique at a takeoff angle of 2°. At this angle the intensity of a reflection was about 90% of the maximum value