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Phenyldiazene Complexes. Structure and Spectra of Chlorodicarbonyl(*cis*-phenyldiazene)bis(triphenylphosphine)ruthenium(II) Perchlorate Methylene Chloride Solvate

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Abstract: The structure of $[RuCl(CO)_2(HN_2C_6H_5)(P(C_6H_5)_3)_2][ClO_4]\cdot CH_2Cl_2$ has been determined by X-ray diffraction methods. The compound crystallizes from methylene chloride as solvated crystals in space group $C_{2h}^5 - P2_1/c$ with four formula units in a cell of dimensions $a = 11.801\ (5)$ Å, $b = 17.752\ (8)$ Å, $c = 22.938\ (11)$ Å, and $\beta = 110.96\ (2)°$. Based on 5074 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure has been solved and refined by full-matrix, least-squares methods to an R index (on F) of 0.053. The structure consists of discrete ions and solvent molecules. The ruthenium cation is six-coordinate, with trans phosphine ligands and cis carbonyl ligands. The phenyldiazene ligand adopts the cis configuration about the N–N double bond and is bound in a σ fashion through N(1) to the metal. The positional parameters of the nonaromatic diazene proton were refined. Important angles and distances are Ru–N(1) = 2.086 (5) Å, N(1)–N(2) = 1.218 (7) Å, N(1)–H = 1.00 (6) Å, N(2)–C(phenyl) = 1.409 (6) Å, ∠Ru–N(1)–N(2) = 129.2 (5)°, ∠Ru–N(1)–H = 128 (4)°, ∠H(1)–N(1)–N(2) = 102 (4)°, and ∠N(1)–N(2)–C(phenyl) = 118.2 (5)°. The short, nonbonded contact between the nonaromatic diazene proton and an ortho-phenyl proton causes considerable rotation of the phenyl group about the N–C bond. Spectroscopic and structural data suggest that phenyldiazene behaves as a normal σ-donor ligand without significant π-bonding characteristics. The N–N stretching frequencies for $PtCl(HN_2C_6H_5)(P(C_2H_5)_3)_2^+$, the title complex, and their respective deprotonated analogs are shown to be coupled with vibrational modes of the phenyl groups. The values of ν(NN) for the diazenido complexes are shown to be lower than those for the corresponding diazene complexes.

Aryldiazo and aryldiazene ligands have been of great interest in recent years because of their close relationship to dinitrogen and nitrosyl ligands. Recent work has shown that diazo ligands can be prepared from coordinated dinitrogen in Re, Mo, and W complexes,[1-3] that diazene ligands can be prepared from diazo ligands by reaction with protic acids,[3-6] and that diazene ligands in Rh and Pt complexes can be reduced under mild conditions using hydrogen in the presence of a catalyst[5,6] to form hydrazine ligands. These reactions suggest the possibility of reducing dinitrogen through this chemical route under mild conditions with the aid of transition metals. Indeed, Parshall and Sutton have suggested that aryldiazene complexes may be useful models for studying the reduction of dinitrogen in synthetic and biological systems.[6,7]

To date, the only other reported structure of a monodentate aryldiazene complex is that of $PtCl(p\text{-}HN_2C_6H_4F)(PEt_3)_2^+$.[8,9] In addition, two other iridium complexes have been studied which contain bidentate *trans*-aryldiazene ligands that have undergone ortho-metalation.[10,11] The ability of transition metals to stabilize through coordination otherwise unstable species is especially evident for aryldiazene complexes as well as for an interesting six-coordinate, rhenium complex which contains an another form (PhNH=N=Re) of phenyldiazene, $ReCl_2(N_2HPh)(NH_3)(PPhMe_2)_2^+$.[12] We now report the crystal structure of the six-coordinate, *cis*-phenyldiazene complex of ruthenium, $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]$, and show that the aryldiazene ligand is conveniently identified using Raman vibrational and nuclear magnetic resonance spectroscopy.

Experimental Section

Crystal Preparation. The title complex was prepared by two independent methods (eq 1, 2) which yielded identical products.

$$RuCl(CO)_2(N_2Ph)(PPh_3)_2 + HClO_4 \xrightarrow{EtOH} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4] \quad (1)$$

$$RuHCl(CO)_2(PPh_3)_2 + [PhN_2][ClO_4] \xrightarrow{Me_2CO} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4] \quad (2)$$

The same complex as the BF_4^- salt has been prepared by another method, eq 3.[5a] A reaction similar to eq 2 was performed using

$$[RuCl(CO)(HN_2Ph)(PPh_3)_3][BF_4] + CO \xrightarrow{Me_2CO} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][BF_4] + PPh_3 \quad (3)$$

$RuHCl(CO)_2(PPr_2Bu)_2$ as a starting material.[5b,8]

Raman, infrared, and NMR spectra show the cationic products to be the same in all three reactions. The yellow product prepared according to reaction 1 was recrystallized from acetone as poorly developed solvent-free crystals and from dichloromethane as beautiful, well-developed prisms of the 1:1 CH_2Cl_2 solvate which lost solvent at the rate of about 10% per day forming the unsolvated powder. At room temperature in the presence of air, the crystals are moderately photosensitive; they become completely black under ambient light conditions in about 2 days. In the absence of air or light, no decomposition was observed. Indeed, at −20° under a nitrogen atmosphere in the dark, no decomposition was observable after 6 months. A suitable crystal of the freshly recrystallized methylene chloride solvate was sealed in a capillary under a methylene chloride atmosphere in order to prevent desolvation. There was no detectable deterioration of crystal quality during data collection. Anal. Calcd for $C_{45}H_{38}Cl_4N_2O_6P_2Ru$: C, 53.64; H, 3.80; N, 2.78; Cl, 14.07. Found: C, 53.61; H, 3.96; N, 2.62; Cl, 14.17. Elemental analyses were performed by H. Beck of Northwestern's Analytical Services Laboratory and by Micro-Tech Laboratories, Inc., Skokie, Ill. Infrared spectra were recorded in hexachlorobutadiene 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 in CD_2Cl_2 with tetramethylsilane as an internal standard. Raman spectra were obtained using a unit containing a Spex 1401 double monochromator and a krypton ion laser. The sample was sealed under vacuum, spun in a 12-mm tube, and cooled to about 190 K in order to reduce thermal decomposition. Power at the sample was about 50 mW using the 6471 Å exciting line. The spectra were calibrated using known laser plasma lines. Using a Faraday balance, we found the complex to be diamagnetic.

The preparative details for reactions 1 and 2 will be reported separately. The complex $[PtCl(HN_2Ph)(PEt_3)_2][PF_6]$ was prepared according to literature methods using benzenediazonium hexafluorophosphate instead of the tetrafluoroborate salt.[13] Although no difficulty was encountered in deprotonating the (*p*-fluorophenyl)diazene complex according to the published procedure, the analogous phenyldiazene complex decomposed via dinitrogen evolution. Benzenediazonium salts were prepared by usual techniques[14] from aniline and sodium nitrite and were carefully recrystallized from acetone–ethanol–diethyl ether in order to remove any traces of halide ion. Aniline-d_5 (99+% ^{2}H) was purchased from Aldrich Chemical Co.; $Na^{15}NO_2$ (95–97% ^{15}N) and aniline-^{15}N (95–99% ^{15}N) were purchased from Stohler Isotope Chemicals.

Chloro(phenyldiazo)bis(triethylphosphine)platinum(II). This compound was prepared by a modification of the published procedure.[6,13] Chloro(*cis*-phenyldiazene)bis(triethylphosphine)platinum(II) hexafluorophosphate (1.00 g) was stirred in 100 ml of freshly distilled diethyl ether for several minutes at 10° until the complex partially dissolved. With stirring, a solution of an appropriate base was slowly and carefully added until all of the solid dissolved, and the solution had changed color from yellow to violet. Care was taken not to add an excess of base; the colored complexes acted as convenient visual indicators. Only two bases were found which gave acceptable results: (1) a concentrated solution of sodium methoxide in methanol or (2) a solution of trimethylamine in diethyl ether. After the base was added, the solution was stirred 3–6 min to complete precipitation of the unwanted hexafluorophosphate salt. The solution was filtered, and the solvent was removed under a stream of nitrogen. The crude product was dried under vacuum for 15 min. The violet solid was recrystallized by dissolving it in 200 ml of freshly distilled pentane, filtering the solution to remove the brown residue, and removing the pentane under a nitrogen stream. Beautiful violet crystals resulted which were dried under vacuum for 5 min. Yield was 60–70%. Anal. Calcd for $C_{18}H_{35}ClN_2P_2Pt$: C, 41.74; H, 6.16; N, 4.90. Found: C, 41.61; H, 6.20; N, 4.69.

Crystallographic Data. Preliminary film data showed $[RuCl(CO)_2(HN_2C_6H_5)(P(C_6H_5)_3)_2][ClO_4]\cdot CH_2Cl_2$ to belong to the monoclinic system with extinctions (*h*0*l*, *l* odd; and 0*k*0, *k* odd) characteristic of the centrosymmetric space group C_{2h}^5-$P2_1/c$. Based on a least-squares analysis of the angular positons of 15 hand-centered reflections in diverse regions of reciprocal space (in the range 19° < 2θ < 30°), accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection. The mosaicity of the crystal was acceptable for the θ–2θ scan technique. The widths at half-height of several strong, low-angle reflections (ω scan, open counter) lay in the range 0.07–0.13°. Data collection was carried out using 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, and all six were found to remain constant within counting statistics during the entire data collection. There was no evidence of crystal decomposition.

Table I. Summary of Crystal Data and Intensity Collection

Compound	$[RuCl(CO)_2(C_6H_5N_2H)(P(C_6H_5)_3)_2][ClO_4]\cdot CH_2Cl_2$
Formula weight	1007.644
Formula	$C_{45}H_{38}Cl_4N_2O_6P_2Ru$
a	11.801 (5) Å
b	17.752 (8) Å
c	22.938 (11) Å
β	110.96 (2)°
V	4487 Å^3
Z	4
Density	1.491 g/cm^3 (calcd) 1.48 (1) g/cm^3 (exptl)
Space group	C_{2h}^5-$P2_1/c$ (monoclinic)
Crystal dimensions	0.60 × 0.32 × 0.27 mm
Crystal shape	Needle in [100] direction, octagonal cross section with {011} faces well developed and {010}, {001} faces poorly developed
Crystal volume	0.0518 mm^3
Temperature	20°
Radiation	Mo (λ(Kα_1) 0.709300 Å) monochromatized from (002) face of mosaic graphite
Transmission factors	0.81 to 0.85
μ	6.99 cm^{-1}
Receiving aperture	4.0 mm wide by 5.0 mm high; 32 cm from crystal
Takeoff angle	1.9°
Scan speed	2° in 2θ/min
Scan range	1.0° below Kα_1 to 1.0° above Kα_2
Background counts	10 sec, 2θ $\leqslant$35°, 20 sec thereafter
2θ limits	3.0–47.0°
Final number of variables	250
Unique data used $F_O^2 > 3\sigma(F_O^2)$	5074
Error in observation of unit weight	2.24 electrons

The intensities of 6952 unique reflections were measured ($k \geq 0$, $l \leq 0$) out to 2θ (Mo Kα_1) = 47.0°. The data were processed in the usual way with $\sigma(F_o^2)$ calculated using a value of 0.04 for *p*.[15] Only the 5074 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.[16] The *R* index for averaging 147 pairs of symmetry-related reflections was 2.0% before the absorption correction was applied and 1.8% afterwards.

Structure Refinement. The structure was solved using a Patterson synthesis to locate the ruthenium atom. Three subsequent refinements and difference Fourier syntheses were required to locate all of the remaining atoms including all 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) converged to *R* indices of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.105$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.146$. During the refinements, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ 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.[17] The anomalous dispersion terms for Ru, P, and Cl were included in F_c.[18] All seven 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 is attached.

After two cycles of anisotropic refinement, a difference Fourier synthesis revealed the previously located phenyl hydrogen atoms, the remaining three hydrogen atoms belonging to the diazene (0.7 e/Å^3), and the solvent (0.6–0.7 e/Å^3). A typical phenyl carbon

Table II. Final Parameters for $[RuCl(CO)_2(HN_2C_6H_5)(P(C_6H_5)_3)_2][ClO_4]\cdot CH_2Cl_2$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.09764 (4)	0.21334 (2)	0.05303 (2)	0.00523 (4)	0.00184 (2)	0.00169 (1)	0.00001 (2)	0.00136 (2)	0.00006 (1)
Cl(1)	0.08449 (14)	0.08010 (9)	0.07273 (8)	0.00770 (15)	0.00253 (5)	0.00285 (4)	0.00004 (7)	0.00207 (7)	0.00030 (4)
Cl(2)	0.38459 (19)	0.10916 (12)	0.31466 (10)	0.01219 (22)	0.00456 (8)	0.00313 (6)	0.00026 (11)	0.00256 (9)	−0.00047 (5)
Cl(3)	−0.1704 (4)	0.0491 (2)	0.3990 (1)	0.0276 (5)	0.0102 (2)	0.0044 (1)	−0.0039 (3)	0.0040 (2)	−0.0003 (1)
Cl(4)	−0.2924 (5)	−0.0596 (2)	0.3089 (2)	0.0466 (9)	0.0075 (2)	0.0067 (1)	0.0018 (3)	0.0031 (3)	−0.0017 (1)
P(1)	−0.07899 (14)	0.23228 (8)	0.08291 (7)	0.00581 (13)	0.00230 (5)	0.00179 (4)	0.00025 (7)	0.00150 (6)	0.00008 (3)
P(2)	0.27146 (13)	0.18718 (8)	0.02415 (7)	0.00557 (13)	0.00217 (5)	0.00174 (4)	−0.00009 (6)	0.00151 (6)	0.00007 (3)
O(1)	0.0986 (5)	0.3721 (3)	0.0129 (3)	0.0127 (6)	0.0029 (2)	0.0051 (2)	0.0007 (3)	0.0047 (3)	0.0009 (2)
O(2)	0.2701 (5)	0.2602 (3)	0.1812 (2)	0.0137 (6)	0.0044 (2)	0.0024 (1)	−0.0014 (3)	0.0006 (2)	−0.0009 (1)
O(3)	0.3286 (7)	0.1572 (5)	0.3421 (4)	0.0199 (10)	0.0145 (6)	0.0066 (3)	0.0043 (6)	0.0026 (5)	−0.0061 (4)
O(4)	0.4899 (8)	0.1377 (5)	0.3115 (5)	0.0220 (12)	0.0092 (5)	0.0127 (5)	−0.0062 (6)	0.0098 (7)	−0.0025 (4)
O(5)	0.4052 (10)	0.0381 (5)	0.3401 (5)	0.0335 (16)	0.0092 (5)	0.0100 (5)	0.0049 (7)	0.0065 (7)	0.0053 (4)
O(6)	0.3027 (7)	0.0950 (5)	0.2522 (3)	0.0223 (11)	0.0109 (5)	0.0039 (2)	0.0027 (6)	0.0025 (4)	−0.0017 (3)
N(1)	−0.0215 (4)	0.1837 (3)	−0.0357 (2)	0.0064 (5)	0.0030 (2)	0.0017 (1)	0.0007 (3)	0.0015 (2)	0.0002 (1)
N(2)	−0.0800 (5)	0.2242 (3)	−0.0788 (3)	0.0098 (6)	0.0038 (2)	0.0023 (1)	−0.0008 (3)	0.0017 (2)	0.0000 (2)
C(1)	0.0976 (6)	0.3159 (4)	0.0276 (3)	0.0062 (6)	0.0034 (3)	0.0027 (2)	0.0005 (3)	0.0025 (3)	0.0000 (2)
C(2)	0.2055 (6)	0.2404 (3)	0.1347 (3)	0.0081 (6)	0.0023 (2)	0.0024 (2)	−0.0003 (3)	0.0021 (3)	−0.0003 (3)
C(3)	−0.3022 (10)	0.0012 (8)	0.3628 (6)	0.0129 (13)	0.0114 (8)	0.0073 (5)	0.0021 (8)	0.0030 (7)	0.0001 (5)
H(1)	−0.050 (6)	0.132 (4)	−0.053 (3)	5.0^c					

Group^d	x_c	y_c	z_c	δ	ϵ	η
1	−0.2608 (3)	0.1624 (2)	−0.1834 (2)	−2.712 (3)	−3.120 (3)	−0.598 (3)
11	−0.1235 (2)	0.4049 (2)	0.1118 (1)	0.210 (3)	2.871 (2)	−1.638 (3)
12	−0.3205 (2)	0.1780 (1)	−0.0280 (1)	−2.741 (2)	−3.167 (3)	−0.537 (3)
13	−0.0846 (3)	0.1487 (2)	0.2055 (1)	1.475 (3)	−3.123 (3)	1.991 (3)
21	0.4389 (3)	0.3349 (2)	0.0425 (1)	−2.123 (3)	−2.437 (3)	3.216 (3)
22	0.1907 (3)	0.1183 (2)	−0.1146 (1)	2.720 (3)	−2.619 (2)	−1.461 (3)
23	0.4713 (2)	0.0695 (1)	0.1059 (1)	−1.671 (6)	1.949 (2)	1.008 (6)

[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] Isotropic thermal parameter (B) which was fixed and not varied. [d] 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 is the diazene phenyl ring.

atom had a height of 2.8 e/Å^3. In addition to the phenyl hydrogen atoms, the solvent hydrogen atoms were also idealized (C–H = 1.00 Å, ∠HCH = 109.5° and H–C–H plane perpendicular to Cl–C–Cl plane). Two additional cycles of anisotropic refinement converged to R = 0.053 and R_w = 0.067. A comparison of $|F_c|$ and $|F_o|$ for the stronger reflections showed no obvious need for an extinction correction. The largest parameter shift in the final cycle of refinement was 0.2σ. The error in observation of unit weight is 2.24 electrons. A final difference Fourier synthesis of residual electron density reveals nothing interesting. Of the ten strongest peaks, one is near the anion (0.8 e/Å^3), one is near the solvent (0.7 e/Å^3), and the remaining eight belong to residuals near various phenyl groups (0.4–0.6 e/Å^3). All but 12 unobserved reflections obey the relation $|F_c^2 - F_o^2| < 4\sigma(F_o^2)$; these fell in the range 4σ–6σ. There are no trends of the quantity $\Sigma w(|F_o| - |F_c|)^2$ 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 and III, and root-mean-square amplitudes of vibration are given in Table IV.[19] A listing of the observed and calculated structure amplitudes for those data used in the refinement is available.[19]

Discussion

General Description of Structure. The structure of $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$ consists of discrete, well-separated ions and solvent molecules. A stereo drawing of the unit cell is shown in Figure 1. The labeling scheme for the cation, together with some bond distances and angles in the inner coordination sphere, is shown in Figure 2. The complex cation has pseudooctahedral geometry with trans triphenylphosphine ligands and cis carbonyl ligands. The three mutually perpendicular coordination planes are well defined: the only significant deviation involves C(1) which is 0.171 (1) Å from the Ru, P(1), P(2), Cl(1), C(1) plane. There are no unusual intermolecular contacts, the shortest being H(114)–H(133) at 2.21 Å, O(4)–H(3) at 2.36 Å, O(6)–H(15) at 2.43 Å, and O(3)–H(22) at 2.46 Å (see Table V).

The Ru–C–O angles differ from 180° by only 1–4°. The bending of the two carbonyls occurs in different directions with no obvious relationship to any of the three coordination planes. The cis disposition of the carbonyl ligands was anticipated on the basis of infrared spectra which show two very strong absorptions at 2076 and 2019 cm^{-1}. The lower energy band is somewhat more intense and is probably assignable to the antisymmetric C–O stretching vibration. The two Ru–C distances are virtually identical, but the C–O distances differ significantly (0.067 (10) Å). The C(2)–O(2) distance is normal but the C(1)–O(1) distance at 1.055 (7) Å is shorter than would be expected. However, we cannot rationalize this shortened distance on the basis of librational motion, impurities, or disorder. Using a riding model, estimates for the librational shortening of the Ru–P, Ru–C, Ru–N(1), Ru–Cl, N(1)–N(2), and C–O distances were made. Both C–O distances increased by about 0.05 Å, all other distances increased by less than 0.01 Å. There are no unusually short nonbonded intramolecular contacts to C(1) or O(1). The infrared and NMR spectral data for the bulk sample from which the data crystal was taken do not show the presence of either isomer of $RuCl_2(CO)(HN_2Ph)(PPh_3)_2$; the chlorine analysis is also satisfactory. Electron density maps show no indication of disorder between Cl(1) and the trans carbonyl.

The metal-ligand distances all fall in the expected ranges. The Ru–P distances at 2.415 (2) and 2.439 (2) Å are typical of such distances for six-coordinate ruthenium complexes containing two trans triphenylphosphine ligands. The Ru–Cl(1) distance at 2.424 (2) Å is slightly longer than the 2.39 Å distances found in several other Ru(II) phosphine complexes, all of which have nonbridging chloro ligands trans to other chloro ligands: $RuCl_2(PPh_3)_3$,[20] 2.388 (7) Å; $RuCl_3(NO)(PPh_3)_2$,[21] 2.394 (2) Å; $RuCl_3(N_2C_6H_4CH_3)(PPh_3)_2$,[21] 2.390 (3) Å; $Ru_2Cl_4(PPhEt_2)_5$,[22] 2.395 (7) Å. However, it is shorter than the

Table III. Derived Positional and Thermal Parameters for Ring Carbon and Hydrogen Atoms

Atom[a]	Carbon x	Carbon y	Carbon z	Carbon B[b]	Hydrogen x	Hydrogen y	Hydrogen z
C(111)	−0.1021 (4)	0.3299 (2)	0.1006 (2)	3.30 (11)			
C(112)	−0.1248 (4)	0.3833 (2)	0.0531 (1)	3.96 (13)	−0.126	0.368	0.011
C(113)	−0.1462 (4)	0.4583 (2)	0.0643 (2)	4.93 (15)	−0.162	0.497	0.030
C(114)	−0.1449 (5)	0.4800 (2)	0.1231 (2)	5.84 (17)	−0.160	0.534	0.131
C(115)	−0.1222 (4)	0.4265 (2)	0.1706 (2)	5.32 (16)	−0.123	0.442	0.212
C(116)	−0.1009 (4)	0.3515 (2)	0.1594 (2)	4.02 (13)	−0.087	0.313	0.193
C(121)	−0.2195 (3)	0.2034 (2)	0.0217 (2)	3.01 (10)			
C(122)	−0.3127 (4)	0.2534 (2)	−0.0097 (2)	3.92 (12)	−0.307	0.307	0.003
C(123)	−0.4137 (3)	0.2281 (2)	−0.0594 (2)	4.80 (15)	−0.479	0.264	−0.083
C(124)	−0.4215 (3)	0.1526 (2)	−0.0777 (2)	4.73 (14)	−0.492	0.135	−0.114
C(125)	−0.3283 (4)	0.1026 (2)	−0.0464 (2)	4.24 (13)	−0.333	0.049	−0.060
C(126)	−0.2273 (3)	0.1279 (2)	0.0034 (2)	3.58 (12)	−0.161	0.092	0.026
C(131)	−0.0818 (4)	0.1808 (2)	0.1504 (2)	3.32 (11)			
C(132)	0.0261 (3)	0.1582 (3)	0.1971 (2)	4.93 (15)	0.105	0.164	0.193
C(133)	0.0233 (4)	0.1261 (3)	0.2522 (2)	6.73 (20)	0.096	0.108	0.286
C(134)	−0.0874 (5)	0.1166 (3)	0.2606 (2)	6.48 (19)	−0.096	0.092	0.299
C(135)	−0.1953 (4)	0.1392 (3)	0.2139 (2)	5.72 (17)	−0.278	0.133	0.218
C(136)	−0.1924 (3)	0.1713 (3)	0.1588 (2)	4.24 (13)	−0.269	0.189	0.125
C(211)	0.3674 (3)	0.2701 (2)	0.0328 (2)	3.18 (11)			
C(212)	0.3319 (3)	0.3298 (2)	−0.0096 (2)	4.16 (13)	0.254	0.327	−0.046
C(213)	0.4035 (4)	0.3946 (2)	0.0001 (2)	5.19 (16)	0.377	0.438	−0.030
C(214)	0.5105 (4)	0.3997 (2)	0.0522 (2)	5.49 (16)	0.562	0.446	0.059
C(215)	0.5459 (3)	0.3401 (2)	0.0946 (2)	5.08 (15)	0.623	0.343	0.132
C(216)	0.4744 (4)	0.2753 (2)	0.0849 (2)	4.11 (13)	0.500	0.232	0.115
C(221)	0.2291 (4)	0.1504 (2)	−0.0550 (1)	3.04 (11)			
C(222)	0.2488 (4)	0.1882 (2)	−0.1039 (2)	4.42 (14)	0.290	0.239	−0.097
C(223)	0.2105 (4)	0.1561 (2)	−0.1635 (2)	5.29 (16)	0.225	0.183	−0.199
C(224)	0.1523 (4)	0.0862 (2)	−0.1741 (1)	5.03 (15)	0.126	0.063	−0.217
C(225)	0.1325 (4)	0.0484 (2)	−0.1252 (2)	4.75 (14)	0.093	−0.002	−0.132
C(226)	0.1709 (4)	0.0804 (2)	−0.0657 (2)	3.67 (11)	0.158	0.053	−0.031
C(231)	0.3789 (3)	0.1175 (2)	0.0699 (2)	2.94 (10)			
C(232)	0.3848 (3)	0.0960 (2)	0.1295 (2)	3.41 (11)	0.322	0.116	0.146
C(233)	0.4771 (4)	0.0480 (2)	0.1655 (1)	3.93 (12)	0.479	0.033	0.208
C(234)	0.5636 (3)	0.0215 (2)	0.1419 (2)	4.21 (13)	0.628	−0.013	0.169
C(235)	0.5578 (3)	0.0430 (2)	0.0823 (2)	3.97 (13)	0.620	0.024	0.067
C(236)	0.4654 (3)	0.0910 (2)	0.0463 (1)	3.47 (12)	0.462	0.106	0.004
C(11)	−0.1661 (4)	0.1904 (3)	−0.1318 (2)	4.61 (14)			
C(12)	−0.2592 (5)	0.2384 (2)	−0.1671 (3)	6.30 (19)	−0.257	0.293	−0.157
C(13)	−0.3538 (5)	0.2104 (3)	−0.2188 (3)	8.48 (25)	−0.420	0.244	−0.245
C(14)	−0.3554 (4)	0.1345 (3)	−0.2351 (2)	7.51 (22)	−0.424	0.113	−0.271
C(15)	−0.2624 (5)	0.0865 (2)	−0.1997 (3)	6.56 (19)	−0.265	0.031	−0.210
C(16)	−0.1677 (4)	0.1145 (2)	−0.1481 (2)	5.31 (16)	−0.101	0.080	−0.122

[a] C(*xy*1) is attached to P(*x*) and located in ring *y*, and the atoms in the ring are sequentially numbered around the ring. [b] Isotropic thermal parameters of the hydrogen atoms are taken as the same as those of the respective carbon atoms to which they are bonded; the units are Å².

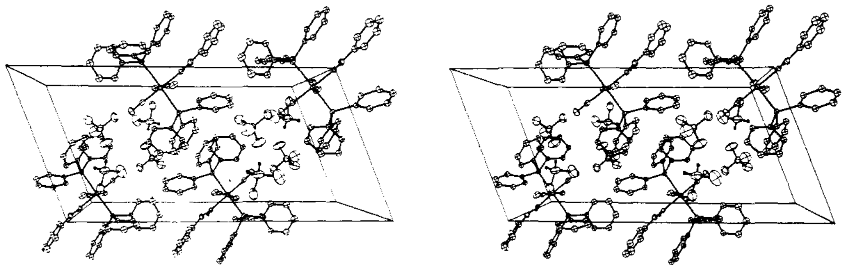


Figure 1. A stereoview of a unit cell of $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$. The *x* axis is almost vertical, the *y* axis is perpendicular to the paper coming toward the reader, and the *z* axis is horizontal to the right. Vibrational ellipsoids are drawn at the 20% probability level. The majority of the hydrogen atoms have been omitted for sake of clarity.

2.444 (7) Å distance found in $RuCl_3(PPhEt_2)_3^-$[23] The Ru-C distances of 1.911 (8) and 1.912 (7) Å are the same as those found in $Ru(C_8H_8)(CO)_3$,[24] 1.908 (8) and 1.924 (6) Å. However, these Ru-C distances are noticeably longer than the 1.77-1.88 Å values for nonbridging carbonyls found in Ru(CO)(EtOH)(TPP),[25] $Ru(CO)(C_5H_5N)$(TPP),[26] $RuCl_4(OH_2)(CO)^{2-}$,[27] $Ru(NH_3)_4(CO)(C_5H_8N_2)^+$,[28] and $Ru(CO)((CF_3)_2C_2S_2)(PPh_3)_2$,[29] and also in several polynuclear ruthenium carbonyl complexes.[30] The Ru-N(1) distance of 2.086 (5) Å is typical of Ru-N(sp^2) distances in $(Ru(C_6H_5N)_4)_2(C_2O_4)^{2+}$ (2.067 (7) Å trans to oxalate and 2.092 (7) Å trans to pyridine):[31] these distances are about 0.05 Å shorter than the Ru-N(sp^3) distances found in similar complexes:[26] $Ru(N_3)(N_2)(en)_2^+$,[32] 2.125 (19) Å; $Ru(en)_3^{3+}$,[33] 2.11 (2) Å; $Ru(NH_3)_6^{2+}$,[34] 2.144 (4) Å; $Ru(NH_3)_6^{3+}$,[34] 2.104 (4) Å.

The intramolecular geometry of the complex is primarily governed by the nonbonded interactions of the phenyldi-

Table V. Selected Distances (Å) and Angles (deg) in $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$

Bond distances		
Ru–C(1)	1.911 (8)	
Ru–C(1)	1.912 (7)	
Ru–N(1)	2.086 (5)	
Ru–Cl(1)	2.424 (2)	
Ru–P(1)	2.439 (2)	
Ru–P(2)	2.415 (2)	
N(1)–N(2)	1.218 (7)	[1.235 (10)][b]
N(2)–C(11)	1.409 (6)	[1.410 (12)][b]
N(1)–H(1)	1.00 (6)	[1.12 (10)][b]
C(1)–O(1)	1.055 (7)	
C(2)–O(2)	1.122 (7)	
P(1)–C(111)	1.822 (4)	
P(1)–C(121)	1.822 (3)	
P(1)–C(131)	1.809 (4)	
P(2)–C(211)	1.824 (4)	
P(2)–C(221)	1.824 (4)	
P(2)–C(231)	1.813 (3)	
Cl(2)–O(3)	1.363 (6)	
Cl(2)–O(4)	1.369 (8)	
Cl(2)–O(5)	1.375 (8)	
Cl(2)–O(6)	1.434 (7)	
C(3)–Cl(3)	1.705 (13)	
C(3)–Cl(4)	1.679 (14)	

Nonbonded distances		
H(1)–Ru	2.82 (6)	
H(1)–H(16)	1.75	[1.71][b]
H(1)–N(2)	1.73 (6)	
N(1)–C(11)	2.256 (6)	
N(2)–C(16)	2.493 (7)	
N(2)–C(12)	2.361 (7)	
N(1)–H(16)	2.62	
N(2)–H(16)	2.72	
N(2)–H(12)	2.53	
P(1)–C(1)	3.169 (8)	
P(1)–C(2)	3.139 (7)	
O(4)–H(3)	2.36	
P(1)–N(1)	3.152 (6)	
P(1)–Cl(1)	3.376 (3)	
P(2)–C(1)	3.090 (8)	
P(2)–C(2)	3.056 (8)	
P(2)–N(1)	3.231 (5)	
P(2)–Cl(1)	3.389 (3)	
C(1)–C(2)	2.686 (8)	
C(1)–N(1)	2.851 (8)	
C(2)–Cl(1)	3.272 (6)	
N(1)–Cl(1)	2.985 (5)	

Bond angles		
P(1)–Ru–P(2)	176.83 (5)	
P(1)–Ru–C(1)	92.7 (2)	
P(1)–Ru–C(2)	91.5 (2)	
P(1)–Ru–N(1)	87.9 (1)	
P(1)–Ru–Cl(1)	87.94 (5)	
P(2)–Ru–C(1)	90.4 (2)	
P(2)–Ru–C(2)	89.1 (2)	
P(2)–Ru–N(1)	91.5 (2)	
P(2)–Ru–Cl(1)	88.90 (5)	
Ru–N(1)–N(2)	129.2 (5)	[125.3 (6)][b]
Ru–N(1)–H(1)	128 (4)	[130 (4)][b]
N(2)–N(1)–H(1)	102 (4)	[100 (5)][b]
N(1)–N(2)–C(11)	118.2 (5)	[120.0 (8)][b]
N(2)–C(11)–C(12)	114.5 (4)	[114.6 (9)][b]
N(2)–C(11)–C(16)	125.4 (4)	[123.3 (9)][b]
Ru–C(1)–O(1)	178.7 (6)	
Ru–C(2)–O(2)	175.9 (6)	
Cl(3)–C(3)–Cl(4)	112.8 (7)	
O(3)–Cl(2)–O(4)	113.1 (6)	
O(3)–Cl(2)–O(5)	114.8 (7)	
O(3)–Cl(2)–O(6)	107.8 (5)	
O(4)–Cl(2)–O(5)	109.7 (6)	
O(4)–Cl(2)–O(6)	108.2 (6)	
O(5)–Cl(2)–O(6)	102.5 (6)	
C(1)–Ru–Cl(1)	173.4 (2)	
C(2)–Ru–N(1)	179.4 (2)	
C(1)–Ru–C(2)	89.3 (3)	
C(1)–Ru–N(1)	90.9 (3)	
C(2)–Ru–Cl(1)	97.3 (2)	
N(1)–Ru–Cl(1)	82.5 (2)	
Ru–P(1)–C(111)	113.9 (2)	
Ru–P(1)–C(121)	112.2 (2)	
Ru–P(1)–C(131)	116.7 (2)	
C(111)–P(1)–C(121)	105.8 (2)	
C(111)–P(1)–C(131)	103.9 (2)	
C(121)–P(1)–C(131)	103.1 (2)	
Ru–P(2)–C(211)	111.7 (2)	
Ru–P(2)–C(221)	112.6 (2)	
Ru–P(2)–C(231)	117.4 (2)	
C(211)–P(2)–C(221)	109.6 (2)	
C(211)–P(2)–C(231)	102.1 (2)	
C(221)–P(2)–C(231)	102.6 (2)	
C(3)–H(3)–O(4)	171	

Interplanar Angles				
Ru–N(1)–N(2) P(1)–Ru–N(1)	80.7 (7)	[72.6 (7)][b]	Ru–P(1)–C(111) P(1)–C(111)–C(112)	62.4 (4)
Ru–N(1)–N(2) Cl(1)–N(1)–Ru	11.1 (7)		Ru–P(1)–C(121) P(1)–C(121)–C(126)	59.9 (4)
N(2)–N(1)–Ru N(1)–N(2)–C(11)	7.9 (5)	[3.3 (6)][b]	Ru–P(1)–C(131) P(1)–C(131)–C(132)	26.1 (4)
N(1)–N(2)–C(11) C(16)–N(2)–C(11)	19.7 (10)	[27.2 (13)][b]	Ru–P(2)–C(211) C(212)–P(2)–C(211)	74.1 (4)
H(1)–N(1)–N(2) N(1)–N(2)–C(11)	3 (5)	[17 (5)][b]	Ru–P(2)–C(221) C(226)–P(2)–C(221)	64.3 (3)
C(11)–C(12)–C(16) Ru–N(1)–Cl(1)	30.3 (3)		Ru–P(2)–C(231) C(232)–P(2)–C(231)	19.1 (3)
P(1)–P(2)[a] C(12)–C(11)–C(16)	30.9 (3)	[44.0 (3)][b]		

[a] Vector plane—normal angle. [b] Corresponding value for $[PtCl(p\text{-}FC_6H_4N_2H)(PEt_3)_2][ClO_4]$; see ref 9.

azene group with the two bulky triphenylphosphine ligands. Both phosphine ligands are bent (~2°) slightly away from the diazene, and the phosphine phenyl groups orient themselves in such a way so as to accommodate the diazene. In doing so, these groups cause the C(2)-Ru-Cl(1) angle to open up to 97.3 (2)°. The atom P(2) has more difficulty reducing close contacts. Ring 22 (see Table II) is the closest phosphine phenyl group to the diazene ligand, and most of the shorter nonbonded contacts result therefrom; the dihedral angles about C(221)-P(2) and C(211)-P(2) are 64.3 (3) and 74.1 (4)°, respectively, resulting in some of the shorter nonbonded intramolecular interactions: H(212)-H(222), 2.07 Å; H(222)-C(212), 2.48 Å; H(216)-C(231), 2.49 Å. Excluding H(1)-H(16), the only other nonbonded contacts in this range are C(2)-H(132) at 2.48 Å and C(112)-H(122) at 2.45 Å. Perhaps the steric crowding could account for the reluctance of $RuCl(CO)_2(HN_2Ph)P_2^+$ to react with hydrogen while $PtCl(HN_2Ph)P_2^+$ readily reacts. However, the six-coordinate complex $RhCl_3(HN_2Ph)P_2$ also readily reacts with hydrogen, and

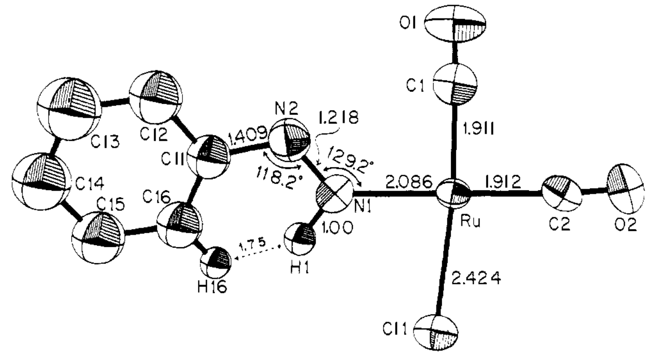


Figure 2. The coordination sphere (triphenylphosphine ligands omitted) with some bond distances and angles for $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]\cdot CH_2Cl_2$. Vibrational ellipsoids are drawn at the 50% probability level, except those for hydrogen atoms which have been artificially reduced.

other factors may be involved.

Surprisingly, there is no evidence for disorder in either the perchlorate anion or the dichloromethane solvent. This might result from the presence of a weak interaction between H(3) of the solvent and O(4) of the anion: H(3)-O(4) = 2.36 Å; H(3)-C(3) = 1.00 Å; C(3)-O(4) = 3.348 (16) Å; ∠C(3)-H(3)-O(4) = 171°. The ClO_4 unit has close to tetrahedral geometry with Cl-O distances which vary from 1.36 to 1.43 Å (average is 1.39 (3) Å) and O-Cl-O angles which vary from 103 to 115° (average is 109 (4)°). The dichloromethane is also well behaved. The Cl-C distances, 1.705(13) and 1.679(14) Å, are not significantly different, and the Cl(3)-C(3)-Cl(4) angle is 112.8 (7)°. In the later stages of refinement, the two hydrogen atoms of the solvent were clearly apparent in the electron density maps and were included in the calculations as fixed contributions. The thermal ellipsoids for the atoms of the anion and solvent are, as expected, distinctly larger than for the corresponding atoms in the large complex cation, but not excessively so.

The Phenyldiazene Ligand. The diazene ligand has definite cis geometry with two sp^2 nitrogen atoms. The hydrogen atom, H(1), attached to N(1) was clearly located in the electron density maps, and its positional parameters were refined. The atom H(1) is located exactly in the Ru-N(1)-N(2) plane on the same side of the N-N double bond as the phenyl group. Atoms H(1) and C(11) are eclipsed with the H(1)-N(1)-N(2)-C(11) dihedral angle equal to 3 (5)°.

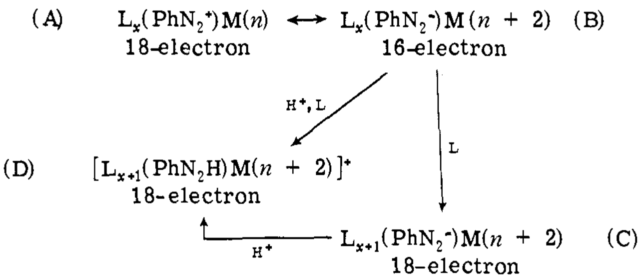
The coordinated *cis*-phenyldiazene has typical bond angles and distances that one would expect for such a moiety; they do not seem to be altered too much as a result of coordination to the metal, and they are similar to those of the (fluorophenyl)diazene ligand in the platinum complex, $PtCl(p\text{-}HN_2C_6H_4F)(PEt_3)_2^+$.[9] Apparently, the diazene ligand adopts the cis configuration in order to accommodate the two bulky groups, Pt and C_6H_5, so that they are trans to each other. Although the structure of $RuCl(CO)_2(N_2Ph)(PPh_3)_2$ is not known as yet, it certainly contains the trans, doubly bent phenyldiazo ligand as do $RhCl(N_2Ph)(ppp)^+$ [8,35] and $PtCl(p\text{-}N_2C_6H_4F)(PEt_3)_2$.[36] Thus, protonation of the doubly bent phenyldiazo ligand[37] (phenyldiazenido) at N(1) causes no basic change in the general geometry of the Ru-N-N-Ph moiety although certain bond distances are likely to be altered. The H(1)-N(1), N(1)-N(2), and N(2)-C(11) distances are 1.00 (6), 1.218 (7), and 1.409 (6) Å, respectively, while the corresponding distances in the platinum structure are 1.12 (10), 1.235 (10), and 1.410 (12) Å.[9] An N-N triple bond in a free ligand is 1.10 Å (from PhN_2^+ and N_2)[38] and a corresponding N-N double bond is 1.24 Å (from PhN_2Ph and HN_2H).[39] In the iridium diazene structures, the N-N distances at 1.27 Å appear to be lengthened because of strain caused by chelation of the ortho-metalated diazene.[10,11] Because of the magnitude of the errors and the paucity of structural data for phenyldiazene complexes, it is difficult to assign any significance to the differences in the H-N or N-N distances between the two diazene ligands in the Ru and Pt complexes.

The conformational angles of the diazene ligand in this Ru complex are strongly governed by two factors, (1) the nonbonded repulsion between H(1) and H(16) whose calculated separation is only 1.75 Å and (2) the nonbonded interactions of the diazene with the two bulky triphenylphosphine ligands. The reduced bulkiness of the triethylphosphine ligands coupled with the lower coordination number causes the second factor to be much less important in the platinum complex. The phosphine ligands in the Ru complex prefer to have the diazene phenyl group slightly canted, but not too much so, with respect to the N(1), Ru, Cl(1), C(1), C(2) plane, while the other ligands in the coordination sphere prevent the diazene from rotating too much about the Ru-N bond. Optimum conjugation between the N-N double bond and the phenyl group is maintained when the N-C-C angles are 120° and the N(1)-N(2)-C(11)-C(16) dihedral angle is zero; but the very short H(1)-H(16) distance of 1.75 Å would become even shorter (about 1.46 Å) under these idealized conditions. Thus, this dihedral angle significantly increases to 19.7 (10)° and the N(2)-C(11)-C(16) angle opens up to 125.4 (4)°. Significantly, there is little increase in the N(1)-N(2)-C(11) angle (118.2 (5)°) or twist about the N-N bond (7.9 (5)°) in order to relieve H(1)-H(16) repulsive interaction. The diazene in the platinum complex has similar bond and conformational angles but it has more freedom to rotate about the N-C and Pt-N bonds in order to relieve any unfavorable nonbonded interactions; furthermore, the hydrogen on N(1) moves out of the N-N-C plane away from the close ortho-hydrogen of the diazene phenyl group.[9]

The preparation of the title complex by reaction 2 involves the insertion of the benzenediazonium cation into the ruthenium-hydrogen bond, and the hydrogen atom is transferred from the Ru where it is about 1.7 Å from the metal to N(1) where it is 2.82 (6) Å from the metal. Although the mechanism of the insertion reaction is not known, the hydrogen atom ultimately must move only by about 1 Å. Such an observation is consistent with the reaction proceeding by a single concerted step.

During the protonation of a doubly bent phenyldiazo group, what changes are likely to take place in the Ph-N-N linkage of the ruthenium complex? Unfortunately, this question cannot be answered in detail because the structure of the neutral, six-coordinate, deprotonated Ru complex (type C) is not yet known. However, certain generalizations can be made. The transition from A to B should be accompanied by a sharp increase in the metal-nitrogen bond distance by about 0.2 Å (Scheme I) and a decrease in the N-N-C angle by about 50°. The transition from B to D should be accompanied by another increase (about 0.1 Å) in the metal-nitrogen distance, a small increase (about 0.02-0.05 Å) in the nitrogen-nitrogen distance, and an increase in the dihedral angle about the N-C bond. Thus, although there appears to be a distinct decrease in the metal-ligand π bonding upon going from A to B, a significant amount of π bonding still seems to be present in doubly bent aryldiazo complexes of type B despite the unfavorable bending at N(1). It appears as though the lone pair on N(1) can interact with the metal and with N(2). In diazene complexes, type D, that lone pair is no longer available, and the

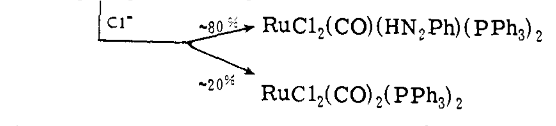
Scheme I



metal-nitrogen distances are in the normal range for metal-nitrogen single bonds. We are studying type C complexes in order to determine if the changes in going from B to D occur upon the addition of a ligand, L, or upon the addition of H^+.

Although only one structure of a doubly bent aryldiazo complex is known in detail, the π-bonding effects noted above seem to cause a small shortening in the M-N and N-N bond lengths in these complexes; indeed, there are some singly bent aryldiazo complexes with longer N-N bond lengths. This is also the case for nitrosyl complexes in which the N-O distances in bent nitrosyl ligands are frequently shorter than those in linear nitrosyl ligands. This is not to say, however, that singly bent (RN_2^+) and doubly bent (RN_2^-) aryldiazo ligands should be classed together as different forms of the same RN_2(neutral) ligand. Although describing the isoelectronic nitrosyl ligand as being essentially neutral has been suggested by some,[40,41] one cannot adopt such a stance for aryldiazo ligands. The RN_2^- ligands readily protonate at N(1), but RN_2^+ ligands protonate less readily, and when they do so, it is at N(2). Complexes such as $RhCl(N_2Ph)(ppp)^+$ [8] are expected to be square pyramidal if they contain Rh(III) since d^6 metals seem to prefer such a geometry,[20,42] but if they contain Rh(I), they are expected to be trigonal bipyramidal since d^8 metals seem to prefer that geometry.[43] We can see no virtue in describing the above complex as containing Rh(II) since this would be an unusual and uncommon low-spin d^7 system about which little is known.

There seems to be no evidence for any trans effects operating in this ruthenium diazene complex. Since the two Ru-C distances are equal, the trans effect of the phenyldiazene ligand is about the same as that of a chloro ligand. Furthermore, a comparison of the Pt-Cl distances in *trans*-$PtCl(HN_2R)(PEt_3)_2^+$ [9] and in *trans*-$PtCl_2(PEt_3)_2$[44] leads to the same conclusion. As was described earlier, the Ru-Cl(1) distance is typical for chloro distances in similar Ru compounds when another chloro ligand is located in the trans position; furthermore, the Ru-N(1) distance is also typical for Ru-N(sp^2) bonds. Thus, the carbonyl ligands exert no significant trans influence on either the chloro or the diazene ligands. If the carbonyls in the Ru-diazene complex do exert a trans effect in the solid state, the effect cannot be any larger than 0.02 Å. This observation is consistent with the reaction of the Ru-diazene complex, reaction 4, with excess halide ion in which either CO or PhN_2H



(4)

can be displaced. However, the absence of a trans effect is in direct contrast to data for another six-coordinate Ru(II) complex, $Ru(CO)(C_5H_5N)(tpp)$,[26] which contains trans carbonyl and pyridine ligands. The Ru-N(pyridine) distance is exceptionally long at 2.193 (4) Å, and the pyridine is known to be quite labile.[45] The difference in the behavior of the two seemingly similar complexes probably is caused by differences between tetraphenylporphyrin and triphenylphosphine, the latter being a strong σ-donating ligand. Indeed, similar to ammonia or pyridine, the σ-bound phenyldiazene ligand seems to behave as though it were a moderately basic nitrogen donor ligand with poor π-accepting characteristics.

Spectral Data. Raman spectra and nuclear magnetic resonance spectra provide two useful and characteristic means for conveniently identifying aryldiazene complexes. Previously Laing et al.[5] and Parshall[6] have utilized NMR for this purpose. Although both techniques are generally useful in identifying aryldiazene complexes, both have certain limitations.[46] Thus, owing to fluorescence, the Raman spectra of $RuCl(CO)_2(HN_2Ph)(PPh_3)_2^+$ are of poor quality, and presumably because of rapid exchange in polar solvents the NMR spectra of $IrCl_2(CO)(HN_2Ph)(PPh_3)_2^+$ do not show the presence of the nonaromatic diazene proton. In both cases, however, the complexes were conclusively identified using one of the spectral techniques which can be applied to a large variety of phenyldiazene complexes. The data for the two complexes whose solid state structures are known are presented here.

The NMR spectra of monodentate phenyldiazene complexes usually show a clear and characteristic resonance for the nonaromatic diazene proton in the region τ −1 to −5 where very few other proton resonances are found; the chemical shift for the corresponding proton in free methyldiazene is τ 5.6.[47] Furthermore, even when the proton is attached to ^{14}N, its resonance is sharp in diazene complexes presumably because of the rapid quadrupolar relaxation of the ^{14}N nucleus as a result of coordination to a metal. The NMR data for the Ru and Pt complexes are tabulated in Table VI, and the spectra for the Ru complex are depicted in Figure 3. As is obvious from the spectra, and the structural results too, the site of attachment of the diazene proton is the nitrogen atom which is also bound to the metal. The one-bond coupling constants between ^1H and ^{15}N are in the range 65-75 Hz. These values are similar to those previously found for coordinated PhN=NH[5,6] and slightly larger than those for free $Ph_2C{=}NH$ (51 Hz),[48] but they are smaller than that expected for a proton attached to an sp^2 nitrogen atom, such as those found in $Ph_2C{=}NH_2^+$ (93 Hz)[47] or in pyrrole (97 Hz).[49] The corresponding two-bond coupling constants for phenyldiazene complexes fall in the narrow range 4-5 Hz. To date no other two-bond coupling constant across an intervening sp^2 nitrogen atom has been measured; however, such coupling constants across sp^2 carbon atoms have been measured, and they seem to have similar magnitudes in *E* isomers of the respective compounds. For the compounds $R_1{}^{15}N{=}CHR_2$ values of $^2J_{NH}$ fall in the range 3-5 Hz for the *E* isomers in which H is cis to R_1 and trans to the lone pair on nitrogen, but they fall in the range 10-16 Hz for the *Z* isomers in which H is trans to R_1 and cis to the lone pair.[50,51] The same trend is observed in the values of $^2J_{NF}$ for the cis and trans isomers of difluorodiazene.[52] By analogy, we expect the presence of a lone pair on N(1) in phenyldiazene to reduce the values of $^1J_{NH}$, and the presence of a lone pair on N(2) trans to the proton attached to N(1) to reduce the values of $^2J_{NH}$. Thus for phenyldiazene and its complexes, the values of the two-bond coupling constants ought to be characteristic of the cis (~4 Hz) or trans (~13 Hz) isomer. As expected, NMR spectra of coordinated $C_6H_5N{=}ND$ show the absence of any resonance in the τ −1 to −5 region. Interestingly, the spectra of $C_6H_5{}^{15}N{=}{}^{14}NH$ complexes distinctly show the coupling of the proton with the ^{15}N atom through two bonds. In the platinum complex, this doublet is poorly resolved because of

Table VI. Proton Nuclear Magnetic Resonance Spectra for the Nonaromatic Proton in Coordinated Phenyldiazene

Compound[a]		Chem[b] shift	$^1J_{NH}$[c]	$^2J_{NH}$[c]	$^2J_{PtH}$[c]
$[PtCl(L)(PEt_3)_2][PF_6]$					
$L = C_6H_5{}^{14}N^{14}NH$	singlet	−4.26			85
$L = C_6H_5{}^{14}N^{15}NH$	doublet	−4.25	74		86
$L = C_6H_5{}^{15}N^{14}NH$	doublet[d]	−4.23		~4	86
$L = C_6H_5{}^{15}N^{15}NH$	two doublets	−4.25	75	4	86
$[RuCl(CO)_2(L)(PPh_3)_2][ClO_4]$					
$L = C_6H_5{}^{14}N^{14}NH$	singlet	−1.75			
$L = C_6H_5{}^{14}N^{15}NH$	doublet	−1.72	65		
$L = C_6H_5{}^{15}N^{14}NH$	doublet	−1.74		4	
$L = C_6H_5{}^{15}N^{15}NH$	two doublets	−1.75	66	4	

[a] Abbreviations: Ph = C_6H_5. Et = C_2H_5. Me = CH_3; solvent is CD_2Cl_2 at ambient temperature. [b] Values given in units of τ with Me_4Si as an internal reference. [c] Coupling constants given in units of Hz. [d] Poorly resolved doublet.

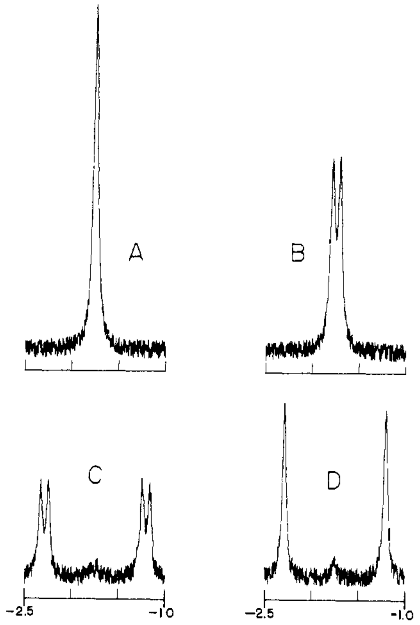


Figure 3. Proton nuclear magnetic resonance spectra for the nonaromatic proton of coordinated *cis*-phenyldiazene in the complex $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]$. Solvent is CD_2Cl_2: A. $Ph^{14}N{=}^{14}NH$; B. $Ph^{15}{=}^{14}NH$; C. $Ph^{15}N{=}^{15}NH$; and D. $Ph^{14}N{=}^{15}NH$.

a small increase in the width of the proton resonances when attached to an ^{14}N atom. The widths at half-height for the proton resonances when attached to ^{15}N are about 3 Hz. When the proton is attached to ^{14}N, the corresponding resonances increase in width by about 10% for the Ru complex and about 50% for the Pt complex.

In an effort to observe the possible nitrogen exchange reaction in solutions of free diazonium salts, reaction 5 was carried out

$$Ph^{15}\overset{+}{N}{\equiv}^{14}N \nrightarrow Ph^{14}\overset{+}{N}{\equiv}^{15}N \qquad (5)$$

using acetone solutions of labeled benzenediazonium hexafluorophosphate which had been allowed to sit at room temperature for 0.5, 2, 4, and 6 hr prior to reaction. To the limit of our sensitivity (less than 6% exchange), NMR spectra showed the presence only of $Ph^{15}N{=}^{14}NH$. Thus under the conditions employed, there was no observable intra- or intermolecular exchange of nitrogen atoms in the free diazonium salt.

The vibrational spectra of monodentate aryldiazene complexes show at least one strong peak in the region of 1450-1525 cm^{-1} which is usually strongly Raman active but weakly infrared active. The value of ν(NN) in free *cis*-diphenyldiazene is 1511 cm^{-1}.[53] Isotopic substitution using ^2H and ^{15}N show that this peak in the phenyldiazene complexes is characteristic of the N=N stretching vibration and that it is strongly coupled with a phenyl vibration in the region of 1440-1445 cm^{-1}. Indeed, in almost all of the spectra two bands are seen to change intensity and frequency upon isotopic substitution. The Raman and infrared data for the Ru and Pt diazene complexes and for the Pt diazenido complex are tabulated in Table VII, and the Raman spectra for the Pt diazene complex are depicted in Figure 4. In this figure, the coupling interaction in the Pt complex can be clearly seen. The normally weak, lower energy band actually becomes the stronger of the two bands when two ^{15}N atoms are present. Applying the same technique used previously for aryldiazo complexes,[54] the two vibrations are mathematically decoupled, and the N=N stretching frequency of 1481 cm^{-1} is found, which is noticeably different from the uncorrected value of 1505 cm^{-1} and significantly different from the values near 1120-1170 cm^{-1} found by Parshall[6] and Cenini et al.[55] for Pt complexes. Although Parshall reports an infrared active band at 1120 cm^{-1} which shifts upon isotopic substitution in the (fluorophenyl)diazene complex, we do not observe any band which shifts upon ^{15}N substitution in this region in the phenyldiazene platinum complexes containing BF_4, PF_6, or ClO_4 anions. Cenini et al.[55] did not verify their spectral assignments using ^{15}N substituted species. Unfortunately our efforts to do so were frustrated by our inability to prepare those complexes by the literature procedure.

Unlike the Pt diazene complex whose N=N stretching vibration is not observed in the infrared spectrum, the corresponding vibration for the Ru diazene complex can be observed in both Raman and infrared spectra. Unfortunately, this vibration is more difficult to observe in the Raman spectra of this Ru complex than in most diazene complexes because the signal-to-noise level is higher owing to fluorescence and because the intensity of the peak corresponding to ν(NN) is only of moderate intensity. Owing to interference of other bands in the infrared spectra and to the poor quality of the Raman spectra, another lower energy band which also shifts upon ^{15}N substitution could not be observed. However, based on our experience, it is probable that the lower energy band is present in the Raman spectra, but it is weaker than that in the Pt diazene complex and is masked by the high background. The approximate shift in energy resulting from coupling can be estimated from (1) the 49-cm^{-1} observed shift and the 53-cm^{-1} calculated shift between the compounds with two ^{14}N atoms and two ^{15}N atoms or from (2) the probable coupling frequency (about 1441 cm^{-}) and approximate intensity ratio (about 4:1) between the 1462-cm^{-1} peak and possible coupling peaks. Both estimations yield shifts in the range of 5-6 cm^{-1}. If coupling is present, it is small, and the uncoupled value for ν(NN) is probably near 1505 cm^{-1} in the Ru diazene complex.

Table VII. Raman and Infrared Spectra in the N=N Stretching Region for Some Phenyldiazene and Phenyldiazenido Complexes

Compound[a]	Observed[b] ν(NN)	$\Delta\nu$(NN)[c]	A', Intensity[d] ratios	E_1^0, Coupling[d] freq	E_2^0, Calcd[d] ν(NN)	ν(NN)[d,h]
$PtCl(L')(PEt_3)_2$						
$L' = C_6H_5{}^{14}N^{14}N$	1439*, 1465 (sh)*[e]	(25, 51)	10:15[g]	1450	1455	1455
$L' = C_6H_5{}^{15}N^{14}N$	1428*, ~1454*[f]	~22	50:10[g]	1450	1432	1456
$L' = C_6H_5{}^{15}N^{15}N$	1405*, ~1454*[f]	~45	100:10[g]	1450	1409	1458
$L' = C_6D_5{}^{14}N^{14}N$	1461*				1461	1461
$L' = C_6D_5{}^{14}N^{15}N$	1438*	23			1438	1462
$[PtCl(L)(PEt_3)_2][PF_6]$						
$L = C_6H_5{}^{14}N^{14}NH$	1417, 1505	(25, 52)	100:249	1443	1479	1479
$L = C_6H_5{}^{14}N^{15}NH$	1413, 1483	26	100:183	1439	1457	1482
$L = C_6H_5{}^{15}N^{14}NH$	1405, 1494	23	100:138	1444	1455	1480
$L = C_6H_5{}^{15}N^{15}NH$	1401, 1470	51	115:100	1439	1432	1482
$L = C_6D_5{}^{14}N^{15}NH$	1422, 1479		100:175	1443	1458	1483
$[RuCl(CO)_2(L)(PPh_3)_2][ClO_4]$						
$L = C_6H_5{}^{14}N^{14}NH$	1511; 1505*					
$L = C_6H_5{}^{14}N^{15}NH$	1487; 1489 (sh)*[f]					
$L = C_6H_5{}^{15}N^{14}NH$	1487; ~1489 (sh)*[f]					
$L = C_6H_5{}^{15}N^{15}NH$	1462; 1462*					

[a] Abbreviations: Et = C_2H_5, Ph = C_6H_5. [b] Frequencies given as wave numbers (cm^{-1}); infrared peaks are denoted by (*); Raman peaks have no annotation; sh = shoulder. [c] The sum of the differences for all of the bands which shift. In parentheses are the calculated shifts for one and two ^{15}N atoms, respectively. [d] See ref 54 for calculations. [e] The phenyl vibration normally at 1477 cm^{-1} shifts to 1482 cm^{-1} in this compound; it also changes intensity slightly. [f] Approximate value. [g] Roughly estimated ratio. [h] The value calculated when two ^{14}N atoms are present.

In order to compare the values of the N=N stretching frequencies before and after protonation in corresponding diazene and diazenido complexes, we reinvestigated the spectral properties of the Pt diazenido complex (see Table VII). Although Parshall reported a value of 1440 cm^{-1} for ν(NN),[6] we were surprised (1) by the apparent absence of coupling between the phenyl modes and ν(NN) in the phenyldiazenido complex, (2) by the relatively large difference between ν(NN) for the (p-fluorophenyl)diazenido complex (1463 cm^{-1}) and that for the phenyldiazenido complex (1440 cm^{-1}), and (3) by the unexpectedly low value of 1440 cm^{-1} compared with the 1455-1475 cm^{-1} values found for several six-coordinate, 18-electron diazenido complexes. We have confirmed Parshall's initial observations; however, we have also shown that significant coupling between the phenyl vibrational modes and ν(NN) occurs. Owing to the presence of a broad, strong, interfering band at 1454 cm^{-1} in the infrared spectra of free and complexed triethylphosphine, the higher energy bands in the phenyldiazenido complexes are difficult to observe. In the complex without isotopic substitution, an obvious shoulder is seen at about 1465 cm^{-1}. In the other cases with ^{15}N substitution, the 1454-cm^{-1} band is clearly observed to increase in intensity. In these latter instances, the resulting uncoupled values of ν(NN) near 1456 and 1458 cm^{-1} are only approximate owing to the difficulty in estimating both the position and relative intensities of the higher energy bands. With no isotopic substitution, the estimation of the intensity and position of the high energy band can be made with more certainty, yet a low value of 1455 cm^{-1} is calculated. Here, however, the low calculated value probably results from an additional coupling interaction with a phenyl mode normally found at 1477 cm^{-1} which anomalously appears at 1482 cm^{-1} in this compound. This same effect also occurs in $IrCl_2(CO)(N_2Ph)(PPh_3)_2$ although the shift of the third band near 1480 cm^{-1} could not be observed because of interference of the phenyl bands in the triphenylphosphine. Indeed, three bands have also been observed to shift in the compound, $OsH(CO)(N_2Ph)(PPh_3)_2$.[54] As has been seen before in other $C_6D_5N_2$ complexes, ν(NN) is decoupled from the perdeuteriophenyl modes, and ν(NN) is found at 1461 cm^{-1} in the Pt complex which is consistent with all of our other findings and expectations. The constancy of the calculated value of the coupling frequency at 1450 cm^{-1} is certainly accidental and not significant. The true value probably lies in the region 1440-1445 cm^{-1}. Because of decomposition, the Raman spectra of the Pt diazenido complex could not be observed.

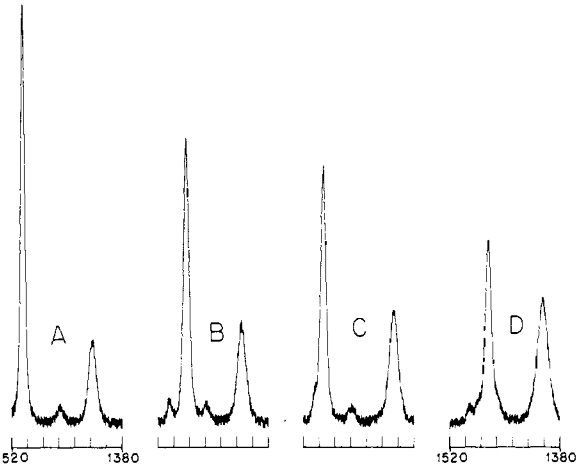


Figure 4. Raman spectra in the N=N stretching region for coordinated *cis*-phenyldiazene in the complex $[PtCl(HN_2Ph)(PEt_3)_2][PF_6]$. Spectra taken in the solid state at 190°K: A, $Ph^{14}N{=}^{14}NH$; B, $Ph^{14}N{=}^{15}NH$; C, $Ph^{15}N{=}^{14}NH$; and D, $Ph^{15}N{=}^{15}NH$.

Concluding Remarks

We can now make some observations about related phenyldiazene and phenyldiazenido complexes. (1) Six-coordinate, 18-electron, phenyldzenido complexes of Ru(II) behave in much the same manner as do square-planar, 16-electron, phenyldiazenido complexes of Pt(II). (2) The uncoupled value of ν(NN) occurs near 1460 cm^{-1} for these diazenido complexes. (3) These complexes react with noncoordinating acids to form phenyldiazene complexes with an accompanying *increase* in the N=N stretching frequency. (4) In contrast, five-coordinate, 16-electron, phenyldiazenido complexes appear to react only with coordinating

$$\begin{array}{ccc} PtCl(N_2Ph)P_2 & \xrightarrow{H^+} & PtCl(HN_2Ph)P_2^+ \\ 1461\ cm^{-1} & & 1481\ cm^{-1} \\ RuCl(CO)_2(N_2Ph)P_2 & \xrightarrow{H^+} & RuCl(CO)_2(HN_2Ph)P_2^+ \\ 1462\ cm^{-1} & & 1505\ cm^{-1} \end{array}$$

acids to form phenyldiazene complexes with an accompanying *decrease* in the N═N stretching frequency. (5) For values of $\nu(NN)$ in the region of 1450–1500 cm^{-1}, there almost always is coupling between the C_6H_5 modes and $\nu(NN)$ in both diazenido and diazene complexes. It appears that the range of the values of $\nu(NN)$ in phenyldiazene complexes is relatively small and that the N═N stretching frequencies themselves are not very sensitive to the overall charge on the complex.

These observations lead us to several conclusions. The metal–nitrogen bond in monodentate aryldiazene complexes primarily involves a σ interaction with little π bonding. Although the π bonding is not as large as that in singly bent aryldiazo complexes, there is a significant π interaction between ligand and metal in many phenyldiazenido complexes. Owing to the presence of the additional ligand, there is a distinct difference between the spectra and chemistry of five-coordinate, 16-electron, phenyldiazenido complexes and those of six-coordinate, 18-electron, phenyldiazenido complexes. In the former case, there is a possibility of a 16-electron ↔ 18-electron equilibrium or interconversion in which a pair of electrons formally resides on the ligand or the metal; but in the latter case, this is not possible because a 20-electron configuration is much less accessible to the complex, and the electron pair must reside on the ligand.

In a manner similar to the copper phenyldiazene complex,[56] the ability to displace the phenyldiazene from the metal in our complexes using Cl^-, CO, MeCN, or a mixture of these suggests the possibility of conveniently preparing small quantities of the isotopically substituted, free diazene under the appropriate conditions. We have already prepared complexes containing $C_6H_5N{=}NH$, $C_6H_5N{=}ND$, $C_6D_5N{=}NH$, and $C_6D_5N{=}ND$, each of which have the isotopically substituted diazo linkages, $-^{14}N{=}^{14}N-$, $-^{14}N{=}^{15}N-$, $-^{15}N{=}^{14}N-$, and $-^{15}N{=}^{15}N-$. We believe that additional structural and synthetic studies will be very useful in understanding and utilizing the phenyldiazene ligand.

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Supplementary Material Available. Table IV, the root-mean-square amplitudes of vibration, and 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 Journals Department, 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 JACS-75-5369.

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Conformational Energy Calculations on Five-Membered Rings in Pentacoordinate Phosphorus[1]

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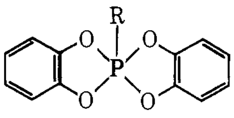
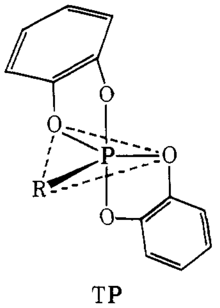
Abstract: It is shown in agreement with X-ray data that the square pyramid (SP) conformation of five-membered ring containing pentacoordinate phosphorus is stabilized relative to the corresponding trigonal bypyramid (TP) when the ring systems are unsaturated and contain highly electronegative heteroatoms directly attached to phosphorus. The primary cause of the stabilization is attributed to ring strain produced by differences in bond lengths which are inherent in the TP form for equatorial vs. apical bonds. For dioxaphospholene compounds examined, ring strain is estimated to be about 3–4 kcal/mol greater in the TP. This enhances the overall stability of the SP conformation relative to the TP form. As the electronegativity of the heteroring atoms is reduced, ring strain effects become less important and the TP appears as the more stable structure in line with structural evidence. The presence of mixed heteroring atoms directly attached to phosphorus and the presence of saturated rings are expected to reduce ring strain differences, thus favoring the formation of the TP, while the presence of four-membered rings will intensify the formation of the SP conformation.

Of the two common isomeric forms for pentacoordinate phosphorus, the trigonal bypyramid (TP) and square pyramid (SP), only the former has been observed for derivatives when simple ligands or monocyclic systems are present.[2-11] The recent appearance of cyclic containing phosphorus compounds, I,[12] bearing structures approximating the SP prompts an examination of the conformational requirements of small membered rings in each of the two idealized environments to ascertain if they are sufficiently different to preferentially stabilize the SP form.

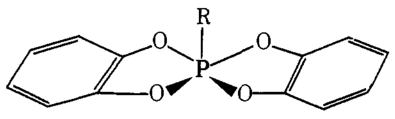


I, R = CH$_3$, F

The dominant consideration[1] appears to center on the presence of two sets of bond properties peculiar to pentacoordinate compounds.[13] In the TP, for the particular type of ring system in I, the P–O bonds would differ substantially in character, while this is not the case for the SP envronment. In the TP, apical bonds are longer than equatorial bonds; whereas in the idealized SP, the four basal bonds would have equal character. Other simple coordination polyhedra do not exhibit this characteristic as can be deduced from geometrical requirements.



TP



SP

In the usual calculation of conformational energies of ring systems, bond distances are frequently held constant as a first approximation with energy minima determined by torsional distortions, angle bending, and van der Waals interactions.[14-18] We will see that bond distance variations enter as a more important term for five-coordinate phosphorus containing planar ring systems. This paper will describe strain effects for these small membered rings resulting from the unequal bond properties and provide an estimate of their magnitude.

Ring Strain Requirements in a TP vs. a SP

A comparison of X-ray data[42] on the SP Ia (R = CH$_3$) with that for the related cyclic system IIa,[6] existing in a TP environment, illustrates possible effects of the change in ring conformation between the two structures.

The differences averaging 0.02 Å between cis PO bond lengths in Ia are evidence of residual TP character as attested by a comparison of the O_1PO_3 and O_2PO_4 angles. These are, respectively, 148.1 and 156.9° showing that oxygen atoms 1 and 3 have some equatorial character while atoms 2 and 4 have some apical character. Likewise, the ring CO bonds have slightly different lengths which bear the same relationship to each other as observed in the TP structure IIa, i.e., a shorter CO bond to an apical oxygen atom compared to the CO bond stemming from an equatorial oxygen. Similar alternations in bond lengths are present in other related systems.[7b,19] With due cognizance of these distortions away from the SP, the oxyphosphorane Ia is highly symmetric relative to the variations in the ring bond lengths seen in the oxyphosphorane IIa. The magnitude of the api-