servation in terms of a lattice consisting of intermolecularly associated units propagating in at least one dimension.[17]

The trimethyl- and triphenyltin(IV) derivatives, on the other hand, fail to yield resolvable spectra at ambient temperatures, even after long counting times. We interpret this negative evidence as ruling out an intermolecularly associated polymeric lattice.

**Structural Conclusions.** While the vibrational spectra for the dimethyltin(IV) derivative fail to provide evidence which can be used to decide the question of the linearity of the carbon–tin–carbon skeleton, the magnitude of the Mössbauer QS and $\rho$ values specify a *trans*-diorganotin, octahedral geometry. The question of bridging vs. chelation is decided, at least tentatively, by the ambient temperature spectrum, and we depict the polymer in the all trans-configuration in structure E. A similar, sheetlike polymeric structure has been proposed for the hypophosphite analogues, $R_2Sn(O_2PH_2)_2$.[13]



E
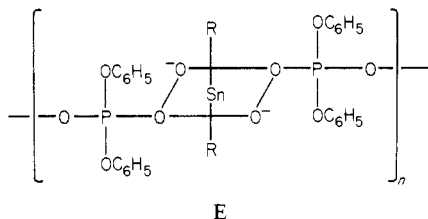
Again, for the triorganotin(IV) derivatives, the $\nu(SnC_3)$ region is obscured but the magnitudes of the Mössbauer QS and $\rho$ values specify a higher than four-coordinated situation at tin, although the absence of resolvable ambient temperature spectra suggest that the value of $n$ in structure B is finite. We have recently solved the structure of (diphenyl phosphato)-

triphenyltin(IV), which forms a solid composed of cyclic hexamers,[23] $[(C_6H_5)_3SnO_2P(OC_6H_5)_2]_6$. The related compound, ($\alpha$-phenyl phosphonato)trimethyltin(IV), which is capable of hydrogen bonding, forms a helical polymer in the solid.[11] Model studies show that the smallest cyclic oligomer capable of incorporating linear O–Sn–O units is the pentamer ($n = 5$ in structure B) whose O–P–O angles would average 108°. In our cyclic triphenyltin(IV) solid, one phenyl group on each tin atom is thrust into the center of the oligomeric ring, which must expand to the hexamer in order to accommodate them.

**Supplementary Material Available:** Tables of mass spectral data (Tables III and IV) and infrared spectral frequencies (Tables V and VI) (6 pages). Ordering information is given on any current masthead page.

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# Chemistry of Bipyridyl-like Ligands. 2. Mixed Complexes of Ruthenium(II) with 2-(Phenylazo)pyridine: A New π-Bonding Probe[1]

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A series of complexes of ruthenium(II) with the strong π-acceptor ligand 2-(phenylazo)pyridine (Azpy), [Ru(Azpy)$_2$(AB)]$^{n+}$, have been prepared. The coligands (AB) include Azpy, 2,2'-bipyridyl, 4,4'-bithiazole, 1,2-diaminoethane, 2,4-pentanedione anion, and X$_2$ (X = NO$_2^-$, CN$^-$, Br$^-$, N$_3^-$, and thiourea). Infrared spectra show the Azpy azo stretching mode to be diagnostic of the coligand (AB) π-accepting behavior, with strongly π-accepting coligands giving the highest Azpy $\nu$(N=N). Visible spectra of the complexes consist of intense charge-transfer bands; the first CT band is not found to be a valid criterion for Ru–ligand π bonding. It is proposed that both σ and π effects are important, causing the observed nonlinear behavior. Emission spectra could be obtained for three of the compounds, one compound appearing to give multiple emissions. Cyclic voltammetry data support the strong π stabilization. Oxidation to Ru(III) could be observed in only a few complexes. However, all reduce at relatively high potentials, with RuAzpy$_3^{2+}$ reducing near 0 V (vs.SCE). A new thin-layer chromatography technique for cationic ruthenium complexes has been developed.

## Introduction

In the first paper of this series,[2] we characterized three isomeric complexes of ruthenium(II) and 2-(phenylazo)-pyridine (Azpy)[3] of the formula [Ru(Azpy)$_2$Cl$_2$]. In these

complexes the ligand azo stretching mode was observed to be considerably shifted (ca. 100 cm$^{-1}$) below the free ligand value; this observation was interpreted as an indication of substantial ruthenium–Azpy π back-bonding. Since the question of the importance of ruthenium–ligand multiple bonding on complex

(1) Presented in part at the 181st American Chemical Society National Meeting, Atlanta, GA, April, 1981; American Chemical Society: Washington, D.C., 1981; INOR 184.
(2) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600.

(3) Other ligand abbreviations used in this paper: bpy, 2,2'-bipyridyl); Btz, 4,4'-bithiazole; en, 1,2-diaminoethane, tu, thiourea; acac, 2,4-pentane-dionate anion, phen, 1,10-phenanthroline.

properties is of current interest, we are pursuing this question further.

It appeared to us to be worthwhile to prepare a series of derivatives of [Ru(Azpy)$_2$(AB)]$^{n+}$; the Azpy stretching mode is found to be diagnostic of the coligand $\pi$-acceptor ability.

## Experimental Section

**Materials.** RuCl$_3$·3H$_2$O was purchased from Mathey Bishop Co., Malvern, PA; all organic solvents and reagents were used as received from Aldrich Chemical. Quaternary salts were purchased from Eastman or J. T. Baker. Azpy was synthesized as reported previously.[2] 4,4'-Bithiazole (Btz) was prepared as described in the literature.[4] Tetrabutylammonium perchlorate was prepared from the bromide and sodium perchlorate in water and recrystallized from acetonitrile–water. Spectrograde solvents were used for spectral and cyclic voltammetric measurements.

**Methods.** Physical measurements were performed as described previously. Luminescence spectra were performed on solid samples immersed in liquid nitrogen; excitation was with the 3371-Å line of an Avco nitrogen laser. The emission was focused on a Jarrel Ash monochromator (0.5 m) and detected by an EMI 9863 QB phototube; the PMT output went to a Keithly 414 picoammeter driving a recorder.

Analyses were performed by Baron Consulting Co., Orange, CT.

All compounds were dried in vacuo over P$_4$O$_{10}$ at room temperature; prior to analysis they were redried at 110 °C.

**Thin-Layer Chromatography.** Thin-layer chromatography was carried out with precoated 0.2-mm EM plates, silica gel 60 with fluorescent indicator (aluminum or plastic backed), or Analtech glass-backed silica gel GHL 0.25-mm thickness without indicator. The GHL plastes were used for applying aqueous solutions. Plates were used without activation.

Chromatograms of the nonelectrolytes were developed with ethanol. For cationic complexes a new procedure was developed since standard developers failed.

Development was carried out with the ascending technique.[5] Plates were cut to 5 × 20 cm dimensions and developed in large screw-cap bottles; upper edges of the flexible backed plates rested against a glass plate, care being taken that the bottom of the TLC plate did not touch the glass plate. TLC plates stood in the developing solvent to a depth of ca. 8 mm. No saturation pad was used as this led to poorer resolution.

Sample solutions were applied to the plates as spots 15 mm from the bottom edge with 1-mm melting point capillaries. A line was scored on the plate at a distance from the origin corresponding to the desired solvent front. Ten centimeters was found to be the optimum distance. (Shorter development did not always give resolution.) Time for development with a 10-cm solvent front was 2 h.

Quaternary salts in absolute ethanol were used as developers, but only two were found to be effective. The best general developer appeared to be 0.5 M tetraethylammonium bromide; occasionally 0.2 M developer provided better resolution. The tetrapropylammonium salt also gave resolution but generally poorer. Tetramethylammonium chloride, tetrabutylammonium bromide, and tetraheptylammonium iodide were unacceptable as each gave low $R_f$ values, poor resolution, and more streaking than the tetraethylammonium developer solutions.

$R_f$ values were found to be reproducible with this technique; 15 plates showed a standard deviation of less than 0.02. After 20 plates had been run in one jar, $R_f$ values began to increase, presumably due to concentration of the developer. Sealed containers of developer appeared to be stable.

Spots on the TLC plates were readily detected by their colors; further sensitivity could be realized or colorless spots detected by utilizing the fluorescent properties of the plates. Occasionally the compounds themselves (e.g., Rubpy$_3$$^{2+}$) could be identified by their characteristic emission under UV light.

In a few cases compounds which should have been clean were found to leave a spot at the origin. So that it could be determined if this was impurity in the compound, a chromatogram was developed on a nonindicating plate. The absence of an origin spot under these conditions indicated the artifact to be due to the indicator.

This method gave excellent results and was also found to be effective for some nonelectrolytes which do not develop with ethanol (e.g., [Rubpy$_2$(NO$_2$)$_2$]).

Analytically pure samples frequently gave more than one TLC spot; this was taken as evidence of the presence of more than one isomer. Our earlier work[2] demonstrated the large difference in TLC behavior of geometric isomers in this series of compounds. Since isomer resolution does not always occur in one solvent, each compound was checked with four developers: 0.2 M and 0.5 M tetraethyl- and tetrapropylammonium salt solutions.

**Preparations. Crude [Ru(Azpy)$_2$Cl$_2$].** A mixture of isomers was prepared as described.[2] A solution of 1.00 g of this mixture in 250 mL of chloroform was stirred with 5.0 g of Al$_2$O$_3$ (grade IV) for 1 h. After filtration and washing with chloroform, the filtrate was evaporated to low volume and precipitated with diethyl ether. This mixture contained all three isomers of [Ru(Azpy)$_2$Cl$_2$] previously described;[2] an impurity which appeared at the origin on TLC was removed by this treatment. This material was used in subsequent preparations.

**[Ru(Azpy)$_2$(NO)$_2$].** A mixture of 2.00 g of crude [Ru(Azpy)$_2$Cl$_2$] and 1.00 g of NaNO$_2$ in 400 mL of absolute ethanol was refluxed for 1$^1$/$_2$ h (very long reflux times (8 h) resulted in extensive decomposition). After the solution cooled to room temperature for 1 day, the dark purple, crystalline product was filtered, washed with water, ethanol, and diethyl ether, and dried; yield 1.49 g (72%). This compound consisted predominantly of one isomer. Recrystallization from chloroform (250 mL/g) adding two volumes of diethyl ether yielded one isomer. Anal. Calcd for [Ru(Azpy)$_2$(NO$_2$)$_2$]: C, 47.22; H, 3.24; N, 20.03. Found: C, 47.50; H, 2.92; N, 20.06.

**[Ru(Azpy)$_2$(CN)$_2$].** A mixture of 0.20 g of [Ru(Azpy)$_2$Cl$_2$] and 0.50 g of KCN in 50 mL of absolute ethanol was heated on the steam bath for 2 h, allowed to cool, and finally cooled in ice. After filtration the bright purple solid was washed with water. For purification the dried sample was dissolved in chloroform and passed through a short (8-cm) Al$_2$O$_3$ (grade IV) column, eluting off with the same solvent, and the solvent was evaporated to ca. 10 mL. Slow addition of a few milliliters of petroleum ether bp 30–60 °C) caused precipitation. The product was filtered, washed with petroleum ether, and dried; yield ca. 0.06 g (31%). TLC showed only one isomer. Anal. Calcd for [Ru(Azpy)$_2$(CN)$_2$]: C, 55.48; H, 3.49; N, 21.57. Found: C, 55.25; H, 3.65; N, 21.73.

**[Ru(Azpy)$_2$(H$_2$O)] Solution.** A solution of an aquo compound was prepared by refluxing 1.00 g of [Ru(Azpy)$_2$(NO$_2$)$_2$] in 200 mL of 1 N H$_2$SO$_4$ for 2$^1$/$_2$ h. After filtration this solution was diluted to 250 mL and used in the following preparations.

**[Ru(Azpy)$_3$](PF$_6$)$_2$.** A 50-mL sample of the above solution and 0.13 g of Azpy were refluxed for 24 h. After filtration 0.50 g of NH$_4$PF$_6$ (in 4 mL of H$_2$O) was added. The resulting solid was filtered and washed with water. The dried compound was dissolved in hot acetone (90 mL), treated with activated charcoal, and filtered and the filter cake washed with two 5-mL portions of acetone. Diethyl ether (30 mL) was added and the mixture allowed to stand for 5 days. The dark brown solid was filtered, washed with diethyl ether, and dried; yield 0.26 g (77%). TLC showed this compound to contain two isomers. Anal. Calcd for [Ru(Azpy)$_3$](PF$_6$)$_2$: C, 42.13; H, 2.89; N, 13.40. Found: C, 42.29; H, 3.02; N, 13.69.

**[Ru(Azpy)$_2$bpy](ClO$_4$)$_2$.** A 50-mL sample of the aquo complex solution and 0.20 g of bpy were refluxed for 24 h. The solution was then made basic with 2.0 g of Na$_2$CO$_3$, cooled, and filtered, and 1.0 g of NH$_4$PF$_6$ (in 8 mL of H$_2$O) was added. After 5 h of standing, the solid was filtered, washed with water, and dried. (This product contained excess bpy.) For purification the compound was stirred with 10 mL of anion-exchange resin (Dowex 21K, 20-50 mesh, Cl$^-$ form) in 20 mL of H$_2$O for 2 h. After filtration the resin was washed with water and the solution made basic with Na$_2$CO$_3$ and after 1 h again filtered to remove any excess bpy. The product was precipitated by the addition of 10 mL of 10% NaClO$_4$ solution and after 1 day was filtered and washed with water and the dark brown solid dried; yield 0.17 g (58%). TLC showed two isomers. Anal. Calcd for [Ru(Azpy)$_2$bpy](ClO$_4$)$_2$: C, 46.72; H, 3.19; N, 13.62; Cl, 8.62. Found: C, 46.84; H, 3.08; N, 13.31; Cl, 8.90.

Similar results (higher yield) were obtained by precipitation as the fluorophosphate salt.

**[Ru(Azpy)$_2$Btz](ClO$_4$)$_2$.** A solution of the aquo complex (25 mL) and 0.040 g of Btz was refluxed for 24 h, cooled, filtered, and precipitated by the addition of 3 mL of 10% NaClO$_4$ solution. After

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1 day the solid was isolated by filtration, washed with water, and dried. Purification was as above, stirring with the Cl⁻ form anion-exchange resin for 1 h. The resulting solution, after resin removal, was heated and 5 mL of 10% NaClO₄ solution added. It was cooled for 1 day and filtered and the dark brown microcrystalline solid washed with water and dried; yield 0.10 g (67%). TLC showed the presence of two isomers. Anal. Calcd for [Ru(Azpy)₂Btz](ClO₄)₂: C, 40.29; H, 2.66; N, 13.43. Found: C, 40.46; H, 2.81; N, 13.52.

**[Ru(Azpy)₂Br₂].** To 50 mL of a solution of the aquo compound was added 1.0 g of KBr and the solution heated on the steam bath 3 h. After cooling at room temperature for 1 day, it was filtered, washed with water, and dried. The sample was dissolved in hot chloroform (30 mL), passed through a short (8-cm) Al₂O₃ column (grade IV), eluted with chloroform, and evaporated to 30 mL. After 210 mL of diethyl ether was added and after the complex was allowed to stand for 4 days, the complex was isolated by filtration, washed with diethyl ether, and dried. It appeared as a purple, crystalline solid with a metallic luster; yield 0.18 g (80%). TLC showed the presence of two isomers. Anal. Calcd for [Ru(Azpy)₂Br₂]: C, 42.12; H, 2.89; N, 13.40. Found: C, 42.01; H, 3.00; N, 13.24.

**[Ru(Azpy)₂en](ClO₄)₂.** A 2-mL sample of 85% en, 10 mL 10% NaClO₄ solution, and 25 mL of the aquo complex solution were heated on the steam bath for 1 h and allowed to cool to room temperature for 1 day. The dark purple-brown compound was isolated by filtration, washed with water, and dried. Purification was as for [Ru(Azpy)₂bpy](ClO₄)₂. Filtration after 1 day, followed by washing with water and drying, yielded 0.07 g (54%). Anal. Calcd for [Ru(Azpy)₂en](ClO₄)₂: C, 39.67; H, 3.61; N, 15.43. Found: C, 39.41; H, 3.77; N, 15.63. TLC showed this compound to be predominantly one isomer with a faint trace of a second isomer.

**[Ru(Azpy)₂(N₃)₂].** A 100-mL sample of the solution of the aquo compound was neutralized with 4 g of Na₂CO₃; 0.40 g of NaN₃ was added and the mixture heated on the steam bath for 2¹/₂ h. On cooling the solution to room temperature, the complex was isolated by filtration, washed with water, and dried. It was dissolved in chloroform (70 mL), passed over a short (8-cm) Al₂O₃ column (grade IV), and eluted with chloroform. The eluate was evaporated to ca. 30 mL and 150 mL of diethyl ether added. After 4 days the complex was isolated by filtration, and the dark purple crystals were washed with diethyl ether; yield 0.23 g (58%). Anal. Calcd for [Ru(Azpy)₂(N₃)₂]: C, 47.90; H, 3.29; N, 30.48. Found: C, 47.94; H, 3.56; N, 30.28. TLC showed the compound to consist of two isomers.

**[Ru(Azpy)₂(tu)₂](ClO₄)₂.** [Ru(Azpy)₂(NO₂)₂] (0.10 g) was refluxed for 1 h in 20 mL of 1 M perchloric acid. After filtration of the hot solution, 0.10 g of thiourea was added and the solution heated on the steam bath. Crystals formed after ca. 30 min, and the solution was allowed to cool to room temperature for 1 day. The dark purple-black crystals were filtered and washed with water; yield 0.13 g (89%). Anal. Calcd for [Ru(Azpy)₂(tu)₂](ClO₄)₂: C, 35.21; H, 3.20; N, 17.11; S, 7.83. Found: C, 35.48; H, 3.42; N, 16.88; S, 8.09. TLC showed the compound to consist of two isomers.

Preparation of this complex in 1 N H₂SO₄ gave a compound showing three components by TLC.

**[Ru(Azpy)₂(acac)]ClO₄.** [Ru(Azpy)₂(NO₂)₂] (0.10 g) was refluxed for 1 h in 20 mL of 1 M perchloric acid, the solution was filtered, and 2.5 mL of aq. NH₃ and 1 mL of 2,4-pentanedione were added. This solution was kept on the steam bath for 3 h; 10 mL of 10% aqueous NaClO₄ was added and allowed to cool to room temperature overnight. The dark purple solid (with a copper luster) was filtered and washed with water before drying; yield 0.09 g (76%). Anal. Calcd for [Ru(Azpy)₂(acac)]ClO₄: C, 48.68; H, 3.78; N, 12.62. Found: C, 48.95; H, 4.07; N, 12.41. TLC showed the compound to consist of two isomers.

As with the thiourea compound, preparation of this complex by dissolving the nitrite in sulfuric acid gave a compound showing three components on TLC. Analysis was acceptable. (Found: C, 48.29; H, 3.98; N, 12.75.)

## Results and Discussion

**Synthesis and TLC.** A number of complexes of the general formula [Ru(Azpy)₂(AB)]ⁿ⁺ (n = 0–2) have been prepared in which the coligands AB vary in their π-acceptor properties. The most general synthetic route was through an aquo complex generated in situ by the reaction of [Ru(Azpy)₂(NO₂)₂] with aqueous acid. While the nitrite complex employed in this

reaction is predominantly one isomer, mixtures of isomers appear in the products. This is not surprising since reaction of isomerically pure [Ru(Azpy)₂(NO₂)₂] with hydrochloric acid produces both α- and β-[Ru(Azpy)₂Cl₂] (both cis, β being the isomer of C₁ symmetry), although the α form predominates. (None of the trans γ chloride is produced in this reaction.) Thus, reaction is accompanied by some isomerization; the results indicate the nitrite complex to be cis, the predominant isomer most likely in the α form. (Starting with pure α-[Ru(Azpy)₂Cl₂] also does not yield the isomerically pure nitrite.)

Some other comments on the chemistry of these compounds are in order. To date we have no evidence for isolable nitrosyl formation in the acid reaction of [Ru(Azpy)₂(NO₂)₂]. This is in contrast to the reaction of [Ru(bpy)₂(NO₂)₂] in acid.[6] With the consideration that Azpy is a stronger π-acceptor than bpy (vide infra), this is not surprising. However, [Ru(Azpy)₂(NO₂)₂] does decompose on prolonged heating in ethanol, although there is no evidence that a nitrosyl is involved in this process.

One route we have investigated as a means of preparing new compounds is the reaction of [Ru(Azpy)₂Cl₂] with silver ion. The chlorides are indeed removed; during the course of the reaction we observe the green trans γ isomer to be the last isomer to lose its chlorides, but displacement does occur. This could be after or during isomerization since the γ form does isomerize under our conditions; it is with interest that we note that Goswami et al.[7] observed that the trans dihalo complexes were unreactive to silver ion

In our continuing efforts to prepare new complexes of "Ru(Azpy)₂", we attempted a reaction between norbornadiene and a mixture of α-, β-, and γ-[Ru(Azpy)₂Cl₂]. No substitution occurred, but the final product was pure α-[Ru(Azpy)₂Cl₂] (the most stable isomer). This may be an easier synthetic technique than the one we have previously reported[2] for the pure α form.

Early in our work it became apparent that some chromatographic procedure was essential in a study of cationic ruthenium complexes. We chose to develop a TLC procedure as a means of analyzing compounds and following reactions because of the speed, economy, and simplicity of the method. No general procedure has been reported for ruthenium compounds; Sullivan et al. have reported a method where Rf values are dependent on sample concentration.[8] Recently Warner and Legg[9] reported a TLC method for cobalt(III) complexes utilizing a triethylammonium bicarbonate buffer mixed with isopropyl alcohol.

Our use of quaternary ammonium salts in ethanol for TLC development is not too different from the Warner and Legg procedure. Our developers, however, are stable with time. The procedure we have described in detail (above) works well for the complexes currently under consideration as well as for ruthenium–bpy compounds. It also gives good development and resolution for some nonelectrolytes.

The compounds reported give excellent analytical values. When TLC shows more than one component, we take this as an indication of the presence of isomers; no attempt has been made in the present work to separate these compounds into their isomers. In general, the different isomers observed on TLC are of the same color, though of differing shades. Some caution is necessary in reaching the conclusion of existence of isomers since on a few occasions we have observed a number

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Table I[a]

**a. Infrared Bands for [Ru(Azpy)₂(AB)] (Bidentate Coligands) (2500–ca. 1300 cm⁻¹)**

| assignt | [Ru(Azpy)₃](PF₆)₂ | [Ru(Azpy)₂bpy](PF₆)₂ | [Ru(Azpy)₂Btz]-(ClO₄)₂ | [Ru(Azpy)₂en]-(ClO₄)₂ | [Ru(Azpy)₂acac]-(ClO₄) |
|---|---|---|---|---|---|
| ring str I | 1604 m | 1606 m | 1604 m | 1607 s | 1600 w |
| ring str II | 1585 m, 1560 w | 1580 w | 1585 w | 1585 w | |
| coligand | | | 1520 w | | |
| ring str III | 1484 m, 1463 m | 1493 w, 1483 w, 1470 w, 1463 m | 1480 w, 1463 m | 1483 w | |
| ring str IV | 1455 s | 1456 sh, 1450 s, 1433 w | 1455 m, 1430 m | 1455 s, 1445 sh | >acac |
| | 1390 w | | 1400 w, 1380 w | | 1385 s, br |
| | 1368 m | 1365 m | | 1375 w | |
| coligand | | | | 1355 s | |
| | | | 1335 w | | |
| | | 1315 w | 1315 m | | 1318 m |
| | 1308 m | 1304 m | 1304 w | 1308 m | |
| N=N | 1358 s | 1348 s | 1363 s | 1325 m | 1300 s |

**b. Infrared Bands for [Ru(Azpy)₂(AB)] (Monodentate Coligands) (2500–ca. 1300 cm⁻¹)**

| assignt | [Ru(Azpy)₂tu₂]-(ClO₄)₂ | [Ru(Azpy)₂-(CN)₂] | [Ru(Azpy)₂-(N₃)₂] | [Ru(Azpy)₂Br₂] | [Ru(Azpy)₂-(NO₂)₂] | [Ru(bpy)₂(NO₂)₂] |
|---|---|---|---|---|---|---|
| coligand | | 2100 s, sp | 2024 s | | | |
| ring str I | 1602 w | 1604 w | 1600 w | 1600 w | 1604 m | 1600 m |
| ring str II | 1585 w | 1591 w | 1585 w, 1545 w | 1585 w, 1550 w | 1587 w | 1567 w, 1556 w |
| coligand | 1515 w | | | | 1468 sh, 1464 sh | 1468 |
| ring str III | 1485 w, 1465 m | 1487 w, 1462 m | 1483 w, 1460 sh | 1482 m, 1456 m | 1483 m, 1463 m | 1488 w |
| ring str IV | 1455 m, 1436 m | 1455 m, 1443 w | 1451 s | 1451 s, 1433 m | 1455 m, 1449 m | 1445 s |
| coligand (NO₂⁻) | | | | | 1445 m | 1424 m |
| | 1404 m | 1404 sh | | | | |
| | 1350 m | | | 1353 w | | |
| coligand | | | | | | 1367 w |
| coligand (NO₂⁻) | | | | | 1358 s | 1338 s |
| coligand (NO₂⁻) | | | | | 1352 s | 1333 sh |
| | | | 1340 w, 1330 w | | | |
| | 1319 w | | 1320 m | | | |
| coligand (NO₂⁻) | | | | | 1317 s | 1310 s |
| | 1306 m | 1303 m | | 1308 w | 1302 sh | 1304 m |
| coligand (NO₂⁻) | | | | | 1307 s | 1288 s |
| N=N | 1331 s | 1387 s | 1294 s | 1326 s | 1369 s | |

[a] Key to band intensities and shapes: s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder.

of components in a product (more than reasonable to expect) and the analysis is acceptable.

**Infrared Spectra.** Earlier[2] we had observed a substantial shift of the Azpy N=N stretching mode in [Ru(Azpy)₂Cl₂] isomers from the free ligand value. This shift was attributed to metal–ligand $\pi$ back-bonding. Thus, the compounds presently under consideration were of substantial interest to determine if the shift of the azo mode was affected by the coligands. All infrared bands (2500–1300 cm⁻¹) are listed in Table I together with assignments. Assignments were made as previously, first locating aromatic ring modes in the 1600–1400-cm⁻¹ region and any major coligand modes (particularly in the 1400–1200-cm⁻¹ region). The azo $\nu$(N=N) could then easily be located in most compounds as the remaining strong band. (We note that Goswami et al. have incorrectly assigned the third aromatic ring mode in *trans*-[Ru(Azpy)₂X₂] as $\nu$(N=N);[7] this further emphasizes the need for a systematic procedure in IR assignments.)

In several complexes this assignment was not immediately obvious. [Ru(Azpy)₂(NO₂)₂] has a number of NO₂⁻ bands in this region. We assumed there should be some correspondence between [Ru(bpy)₂(NO₂)₂] and our nitrite complex. Comparing spectra of the two it becomes clear that $\nu$(N=N) must be one of the three strong bands located at 1369, 1358, and 1352 cm⁻¹, two of which appear to be $\nu_{as}$(NO₂⁻) but shifted from those in [Ru(bpy)₂(NO₂)₂]. We chose the highest as the azo mode to achieve the best correlation with the bpy complex.

[Ru(Azpy)₂en](ClO₄)₂ also has interferences in the region of interest; the CH₂ rock, NH₂ rock, and CN stretch all couple strongly in this region,[11] complicating assignments. Choosing 1355 as an NH₂ mode we are left with the azo stretch at 1325 cm⁻¹.

Assigned values for $\nu$(N=N) (Table I) show a striking but very reasonable trend. As the employed coligand becomes a better $\pi$ acceptor, there is competition for the ruthenium $t_{2g}$ electrons and less $\pi$ back-donation to azpy raising the azo bond order. Thus, with a very strong $\pi$-acid coligand, the azo mode could approach the free ligand value, while with a $\pi$-base coligand a single bond order might be approached for the azo linkage (ca. 1200 cm⁻¹).

We have already noted the stronger $\pi$ bonding in Azpy complexes than in the bpy compounds.[2] $Ru(Azpy)_3^{2+}$ does indeed contain a higher azo mode than does [Ru-(Azpy)₂bpy]²⁺. Both CN⁻ and NO₂⁻ are recognized as important $\pi$-accepting ligands, and both show relatively high values for this mode. Interestingly, acac⁻ falls very low in the sequence. It is possible that this coligand displays some $\pi$-donor behavior, but we do not feel it is possible to argue this point convincingly. However, pronounced coligand $\pi$-acceptor behavior probably does not occur in complexes with azo modes below 1331 cm⁻¹ ([Ru(Azpy)₂(tu)₂](ClO₄)₂), and a considerable range is observed below this point suggesting this possibility.

Coligand modes in the cyano and azido complexes are supportive of this argument. For [Ru(Azpy)₂(CN)₂], $\nu$(CN)

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**Table II.** Visible Spectra of [Ru(Azpy)₂(AB)]ⁿ⁺

| compd | λmax, nm (10⁻³ε,[a] M⁻¹ cm⁻¹) | | | | | | |
|---|---|---|---|---|---|---|---|
| Azpy | | 440 (0.39) | | 318 (13.7) | | 227 (9.7) | |
| Ru(Azpy)₃²⁺ [b] | | 498 (13.5) | 470 sh | 377 (37.9) | 323 (20.4) | 277 (22.0) | f |
| Ru(Azpy)₂Btz²⁺ [c] | | 515 | 488 sh | 372 | | 273 | 247 |
| Ru(Azpy)₂bpy²⁺ | | 517 (11.6) | | 374 (25.3) | 320 (23.1) | 284 (34.3) | 245 (23.9) |
| Ru(Azpy)₂en²⁺ [c] | | 537 | 515 sh | 363 | 309 | 290 | 238 |
| Ru(Azpy)₂(NO₂)₂ | | 538 (9.93) | 457 (3.26) | 355 (19.0) | 313 (23.4) | 288 (17.2) | |
| Ru(Azpy)₂acac⁺ | 657[e] | 565 (12.1) | 484 (3.60) | 361 (22.0) | 326 (24.2) | 261 (17.9) | |
| Ru(Azpy)₂(CN)₂ | 695 (0.5) | 577 (16.4) | 542, 497 sh | 388 sh | 334 (14.3) | 297 (16.0) | 232 sh |
| Ru(Azpy)₂(tu)₂²⁺ [d] | | 585 (6.42) | 496 (3.16) | 342 (16.1) | 306 (19.6) | | |
| Ru(Azpy)₂Br₂ | | 590 (8.41) | 558 sh, 477 (2.25) | 380 sh | 322 (25.3) | | |
| Ru(Azpy)₂(N₃)₂ | | 615 (7.17) | 520 (3.78) | | 330 (23.4) | 240 (31) | 233 (31) |

[a] Molar extinction coefficient.  [b] All ca. 5 × 10⁻⁵ M in CH₂Cl₂ except as noted.  [c] Solubility too low for meaningful ε determination.  [d] In CH₃CN.  [e] Weak, unresolved shoulder.  [f] Most compounds have a high-energy band at the limit of the experimental conditions, which is not reported.

appears as a single strong sharp peak at 2100 cm⁻¹. Schilt[12] has observed in [M(bpy)₂(CN)₂] an increasing splitting of $\nu$(CN) progressing from Fe(II) to Ru(II) to Os(II) and a lowering of the wave number values (2070, 2053 cm⁻¹ for Ru(II)). He has suggested increasing $\pi$ bonding as the reason. Thus, the observed $\nu$(CN) in [Ru(Azpy)₂(CN)₂] suggests less $\pi$ acceptance by CN⁻ in this compound than in the bpy analogue and conversely more $\pi$-acidity in Azpy than bpy as our data suggest. (This is not to be confused with the fact that CN⁻ is still a strong $\pi$ acceptor in [Ru(Azpy)₂(CN)₂].)

In the azido complex, [Ru(Azpy)₂(N₃)₂], the antisymmetric N₃ stretch appears at 2024 cm⁻¹ as a strong band, perhaps containing several components. This value suggests equivalent N–N bonds[13] (ionic character) or little Ru–N $\pi$ back-bonding, consistent with our observation of a low azo mode in the complex.

The observed sensitivity of the azo mode to the nature of the coligand causes us to propose the Ru(Azpy)₂ "core" as a valuable new probe for $\pi$-bonding ligands in ruthenium(II) chemistry. By preparing the compound [Ru(Azpy)₂(AB)]ⁿ⁺ and locating the azo mode, the coligand, AB, can be placed in a $\pi$-acidity series. We feel this probe to be a relatively "pure" $\pi$-bonding probe, with little dependence on $\sigma$ effects.

In a recent report Shur et al.[14] have observed a short Ru—N bond and a lengthened N=N distance consistent with a ruthenium(II)–azo $\pi$ back-bond. Their complex exhibits an azo mode lowered 89 cm⁻¹ below the free ligand value. These data certainly lend support to our assertion of the "Ru(Azpy)₂" azo mode being indicative of the degree of Ru–N $\pi$ bonding. Also, Schramm and Ibers[15] have studied diazo complexes of ruthenium(0). They find the N=N bonded in the $\eta^2$ fashion, $\pi$ bound, and conclude the Ru–azo interaction to be electron donation from metal to ligand. A pronounced lowering of $\nu$(N=N) is indeed observed. In the Ru(Azpy)₂ system we have not yet found reasonable arguments to support, nor disprove, $\eta^2$ bonding; a crystal structure must be the ultimate proof of the exact bonding mode. However, our conclusions are not affected by this.

Infrared probes of metal–ligand $\pi$ bonding are not unknown. However, the majority of these have been for organometallic compounds (see, for example, the extensive study of Ittel[16]) and not for the more classical ligands covered in the present study.

**Table III.** Comparison of CT Band Energies and $\nu$(N=N)

| coligand in Ru(Azpy)₂(AB) | $\nu$(N=N), cm⁻¹ | 10⁻³E,[a] cm⁻¹ | Ru(bpy)₂(AB), 10⁻³E,[b] cm⁻¹ |
|---|---|---|---|
| CN⁻ | 1387 | 17.3 | 21.7 |
| NO₂⁻ | 1369 | 18.6 | 22.8 |
| Btz | 1363 | 19.4 | |
| Azpy | 1358 | 20.1 | |
| bpy | 1348 | 19.3 | 22.1 |
| en | 1325 | 18.6 | 20.4 |
| tu | 1331 | 17.1 | |
| Br⁻ | 1326 | 16.9 | 18.4 |
| acac⁻ | 1300 | 17.7 | 19.7 |
| N₃⁻ | 1294 | 16.3 | |

[a] First CT band.  [b] First CT band; data taken from ref 18.

**Table IV.** Emission Bands from [Ru(Azpy)₂(AB)]²⁺ Solids at 77 K

| | λmax, nm | 10⁻³(Stokes shift), cm⁻¹ |
|---|---|---|
| [Ru(Azpy)₃](PF₆)₂ | 764[a] | 7.0 |
| [Ru(Azpy)₂bpy](PF₆)₂ | 829[b] | 7.2 |
| [Ru(Azpy)₂Btz](ClO₄)₂ | 755 | 6.2 |
| | 822 | 7.2 |

[a] Professor Pat Hoggard observes this at 10 K, at 772 nm.  [b] This he observes at 806 nm.

One point must be borne in mind while considering any infrared bonding study: while wave number values may appear to be diagnostic, it is the force constant which gives fundamental bonding information. Calculating force constants requires far more information on the molecular structure than we generally have available. It is then necessary to use an approximation method (such as the Cotton–Kraihanzel technique[17]). We feel use of $\nu$(N=N) in place of the force constant to be a very reliable approximation in the present series of compounds. All of the complexes appear to be the cis isomers (of either $C_1$ or $C_2$ symmetry, or mixtures of these). The only changing component in the infrared experiment is the coligand. Since the coligand is separated from the probe group by two bonds through a heavy atom, effects of different reduced masses should be minor.[17] Thus, we maintain that the azo mode is indeed a reasonable substitute for the force constant in this series of compounds.

**Optical Spectra.** Absorption spectra of solutions of the compounds are reported in Table II. All appear to be typical charge-transfer (CT) spectra with extinction coefficients for the lowest energy band near 10⁴ M⁻¹ cm⁻¹. One compound, ([Ru(Azpy)₂(CN)₂]), has a weak band at lower energy than

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**Table V.** Cyclic Voltammetry Data on Ru(Azpy)$_2$(AB)$^{n+}$ Compounds (Scan Rate = 0.1 V/s)

| | | $E$, V (vs. SCE) (peak separation, mV)$^a$ | | | |
|---|---|---|---|---|---|
| compd | III → II | II → reduced species | | | |
| [Ru(Azpy)$_2$(CN)$_2$]$^b$ | | −0.48 (80) | −1.04 (80) | | |
| [Ru(Azpy)$_2$(NO$_2$)$_2$]$^b$ | | −0.46 (80) | −0.98 (90) | −1.6 (irr) | |
| [Ru(Azpy)$_2$Btz](PF$_6$)$_2$$^c$ | 1.8 (130)$^e$ | −0.43 (120) | −0.94 (100) | | |
| [Ru(Azpy)$_3$](PF$_6$)$_2$$^b$ | | 0.06 (90) | −0.30 (80) | −0.89 (90) | −1.53 (100) |
| $^c$ | | −0.09 (100) | −0.40 (130) | −0.87 (130) | |
| [Ru(Azpy)$_2$bpy](PF$_6$)$_2$$^b$ | | −0.07 (100) | −0.61 (100) | −1.41 (120) | −1.76 (150) |
| $^c$ | | $d$ | −0.70 (160) | | |
| [Ru(Azpy)$_2$en](ClO$_4$)$_2$$^c$ | | −0.31 (120) | −0.91 (80) | | |
| [Ru(Azpy)$_2$tu$_2$](ClO$_4$)$_2$$^c$ | 1.14 (130) | −0.32 (150) | | | |
| [Ru(Azpy)$_2$Br$_2$]$^b$ | 1.19 (80) | −0.54 (80) | −1.0 (irr) | | |
| [Ru(Azpy)$_2$acac](ClO$_4$)$^b$ | 1.54 (130) | −0.38 (130) | −0.97 (100) | −1.86 (irr) | |
| [Ru(Azpy)$_2$(N$_3$)$_2$]$^b$ | 0.96 (130) | −0.52 (100) | −0.98 (120) | −1.7 (irr) | |

$^a$ Ru(bpy)$_3$(ClO$_4$)$_2$ used as reference, giving a peak separation of 120 mV (0.001 M in CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium perchlorate) and peak separation of 80 mV (0.002 M in CH$_3$CN with 0.1 M NaClO$_4$). $^b$ Ca. 0.001 M in CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium perchlorate. $^c$ Ca. 0.002 M in CH$_3$CN with 0.1 M NaClO$_4$. $^d$ Peak not resolved. $^e$ Questionable peak.

the first CT transition, and another ([Ru(Azpy)$_2$(acac)]ClO$_4$) shows a low-energy shoulder on the first CT band; these could be of d–d origin. We assume the first CT band to be Ru (t$_{2g}$) → Azpy ($\pi^*$).

A very interesting trend appears in the locations of the first CT bands. In Table III we have listed data for $\nu$(N═N) and the first CT band energies for Ru(Azpy)$_2$(AB) and Ru-(bpy)$_2$(AB).[18] It will be seen that the ordering of these energies is the same for both the azpy and the bpy series. However, as the degree of Ru–Azpy $\pi$ bonding increases (as evidenced by decreasing $\nu$(N═N)), the RuAzpy CT band reaches a *maximum* in energy and then decreases. A similar trend is seen in the bpy complexes although insufficient data are available for it to be obvious.

The CT band energy should be indicative of the metal–ligand interaction. As the t$_{2g}$ set becomes more stabilized by this interaction, the metal t$_{2g}$–ligand $\pi^*$ separation will increase, assuming the $\pi^*$ level at constant energy. Thus, one anticipates CT band energies to be somewhat in the order of the classical spectrochemical series. Some workers have related the CT energy to metal–ligand $\pi$ bonding.[19] And it is well-known that the spectrochemical series correlates reasonably well with ligand $\pi$-bonding ability.[20]

However, the ligand field interaction is known to be the result of a number of components, two of which are $\sigma$ and $\pi$ effects. As arranged in Table III, the data indicate that the $\pi$ effect reaches a maximum in its influence on the CT band energy well before the Ru–Azpy $\pi$ bonding reaches a maximum. Thus, in [Ru(Azpy)$_2$(CN)$_2$] (having the highest $\nu$-(N═N) observed and thus the lowest degree of Ru—Azpy $\pi$ bonding), the CT energy is quite low. This energy increases to a maximum at [Ru(Azpy)$_3$](PF$_6$)$_2$ and then diminishes. At [Ru(Azpy)$_2$en](ClO$_4$)$_2$ all $\pi$ bonding must be only Ru–Azpy, but the CT energy continues decreasing in the remaining compounds as $\sigma$ effects diminish. [Ru(Azpy)$_2$(acac)](ClO$_4$) again appears to be anomalous, suggesting the presence of a different interaction.

Thus, having a qualitative scale for $\pi$ bonding allows us to rationalize the variation in CT energies. It also indicates that the M–L CT energy is a very risky criterion for M–L $\pi$ bonding.

Emission spectra could only be obtained for three of the compounds. We presume that others emit but too far into the

red for our phototube to detect. Table IV summarizes the data.

Two important points emerge. First, while the Stokes shifts for known ruthenium bipyridyl complexes are ca. 5 × 10$^3$ cm$^{-1}$, the present compounds have emissions shifted by 7 × 10$^3$ cm$^{-1}$. We feel that Azpy is a less rigid ligand than bpy, and the excited-state complex suffers greater distortion along some ligand vibrational coordinate than is possible in bpy complexes. Thus, in the design of compounds exhibiting high-energy CT excited states, a more rigid ligand system may be required.

However, an alternative explanation should also be considered. Recently Kober et al.[21] have examined emission lifetimes of several osmium(II) complexes. As stronger $\pi$-accepting ligands (L) are bonded to Os(bpy)$_2$L$^{2+}$ or Os-(phen)$_2$L$^{2+}$, the emission lifetimes increased. Their data also indicate the Stokes shift to increase. Thus, the Stokes shift could be related to M–L $\pi$ bonding in some fashion we do not yet recognize.

A second important feature is apparent in the emission spectrum of [Ru(Azpy)$_2$Btz](ClO$_4$)$_2$. Two well-resolved, broad bands are present in this emission, separated by ca. 1 × 10$^3$ cm$^{-1}$. This compound is a mixture of two isomers; we do not anticipate such a large difference in the emission of the two geometric isomers since previous observations on CT emission do not indicate such a pronounced isomer dependence.[22]

Since neither [Ru(Azpy)$_3$](PF$_6$)$_2$ nor [Ru(Azpy)$_2$bpy](PF$_6$)$_2$ emissions exhibit structure we do not favor that explanation here. We suggest that the [Ru(Azpy)$_2$Btz](ClO$_4$)$_2$ emission is multiple state, both the Azpy $\pi^*$ and the Btz $\pi^*$ systems emitting. (Emission from [Ru(Btz)$_3$]$^{2+}$ has been reported.[23])

Convincing evidence has been reported for the existence of multiple emissions from ruthenium(II) (although not simultaneous emissions) by Sullivan et al.[24] We hope to gain more insight into this interesting phenomenon in the future.

**Cyclic Voltammetry.** Results of cyclic voltammetry experiments are summarized in Table V. For only a few of the complexes could the Ru(II) → Ru(III) oxidation be observed, the peak presumably appearing above the point of solvent oxidation. [Ru(Azpy)$_2$Btz]$^{2+}$ shows an indication of oxidation near an applied potential of 1.8 V (vs. SCE), but most of the

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compounds are too stabilized for oxidation to be observable. This is a further indication of the strong $\pi$-acceptor behavior of Azpy.

Only in some compounds where the coligands are not $\pi$-acceptors, and total $\pi$-stabilization is through the two Azpy ligands, is oxidation observed. The range of values lends confidence to the conclusion that it is a ruthenium-centered oxidation we are observing and not ligand oxidation.

Many workers have attributed increasing $Ru^{3+/2+}$ potentials to ML $\pi$ bonding;[25] Dose and Wilson[26] have used potential measurements to rank the $\pi$-acceptor behavior of ligands. However, other factors such as $\sigma$ effects and solvation energies are also important, as noted by Cloninger and Callahan.[27] Thus, in $[Ru(Azpy)_2en]^{2+}$ ruthenium(II) is greatly stabilized in spite of the fact that all $\pi$ interaction must be with the two Azpy ligands. In this series of compounds, the potential data are not a quantitative probe for $\pi$ bonding.

A far more interesting situation arises in the reduction potential data, for reduction of the ruthenium(II) complexes. All are reduced at potentials more positive than $-0.6$ V (vs. SCE). In fact, $Ru(Azpy)_3^{2+}$ is reduced to "$Ru(Azpy)_3^+$" at the highest potential yet observed for a ruthenium(II) complex; aqueous $SnCl_4^{2-}$ easily reduces the compound (this chemistry will be reported later).

It is well-known that $Ru(bpy)_3^{2+}$ undergoes reduction; Baxendale and Fiti first observed the formation of reactive,

transient $Ru(bpy)_3^+$.[28] Using the stronger $\pi$-acceptor ligand 2,2'-bipyrazyl, Crutchley and Lever[29] observed the ruthenium(II) tris complex to be reduced at a much more positive potential ($-0.86$ V) than $Ru(bpy)_3^{2+}$. We feel the high reduction potentials we observe for Ru(Azpy) complexes are further verification of the very strong $\pi$-acceptor behavior of the ligand Azpy.

**Registry No.** $Ru(Azpy)_2(NO_2)_2$, 80697-51-4; $Ru(Azpy)_2(CN)_2$, 80697-52-5; $[Ru(Azpy)_3](PF_6)_2$, 80697-54-7; $[Ru(Azpy)_2bpy](ClO_4)_2$, 80697-56-9; $[Ru(Azpy)_2Btz](ClO_4)_2$, 80697-58-1; $Ru(Azpy)_2Br_2$, 80735-95-1; $[Ru(Azpy)_2en](ClO_4)_2$, 80697-60-5; $Ru(Azpy)_2(N_3)_2$, 80697-61-6; $[Ru(Azpy)_2(tu)_2](ClO_4)_2$, 80697-63-8; $[Ru(Azpy)_2(acac)](ClO_4)$, 80697-65-0; $Ru(Azpy)_2Cl_2$, 80735-96-2; $Ru(bpy)_2(NO_2)_2$, 29241-01-8.

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# The Role of d Orbitals on Phosphorus in the Bonding of P(CH₃)₃ and P(CF₃)₃

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The optimum P–C bond lengths of $P(CH_3)_nH_{3-n}$ and $P(CF_3)_nH_{3-n}$ ($n = 1–3$) were determined by ab initio SCF MO calculations with STO-3G and STO-3G* basis sets. Our study shows that the P–C bond of $P(CF_3)_nH_{3-n}$ is longer than that of $P(CH_3)_nH_{3-n}$ regardless of whether d orbitals are present on phosphorus or not and that the role of phosphorus d orbitals in the bonding with carbon orbitals is not counterintuitive but normal.

Instances of anomalous orbital interactions have been observed in extended Hückel and ab initio SCF MO calculations[1-4] and have been discussed under the name of either altruistic covalent interaction[1] or counterintuitive orbital mixing.[2-4] An experimentally observable consequence of counterintuitive orbital mixing might be an unusual bond lengthening that occurs when a bond between electropositive atoms is surrounded by electronegative ligands.[1,4] Marsden and Bartell[1] observed that the P–C bond in $P(CF_3)_3$ is substantially longer than that in $P(CH_3)_3$ and suggested from their extended Hückel calculations that the unusually long P–C bond in $P(CF_3)_3$ arises in part from a counterintuitive interaction of d orbitals on phosphorus with carbon orbitals. Thus,

d orbitals on phosphorus are regarded to play the role of bond lengthening.

It was recently shown by Collins et al.[5] that, in the accurate description of molecules with second-row atoms, d orbitals on second-row atoms play an important role. They found that geometries of molecules containing second-row atoms are well reproduced by a minimal basis set, when supplemented with d orbitals on second-row atoms. For example, two-heavy-atom bond lengths calculated by STO-3G* basis sets are generally shorter than those calculated by STO-3G basis sets and are in better agreement with experimental values. Thus, d orbitals on second-row atoms play the role of bond shortening.

Concerning the role of d orbitals on phosphorus, therefore, the conclusion of Marsden and Bartell is not consistent with that of Collins et al. To resolve this discrepancy, we have determined the optimum P–C bond lengths in $P(CH_3)_nH_{3-n}$

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