Fourier program, the AGNOST absorption program, and Busing and Levy's ORFFE function and error program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. The diffractometer was run under the disk-oriented Vanderbilt system (P. G. Lenhert, *J. Appl. Cystallogr.*, **8**, 568 (1975)).
(15) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A; D. T. Cromer, *ibid.*, Table 2.3.1.
(16) See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
(17) W. C. Hamilton, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 4.2.
(18) Supplementary material.
(19) For the complexes $M(NO)_2(PPh_3)_2^+$ (M = Co, Rh, Ir) we have noted a correlation between the average corrected nitrosyl stretching frequency $\nu_{av}'$ (ref 10) and the M–N–O angle, $\omega$. This correlation is given by the unit-weighted least-squares line $\omega$ (deg) = $0.231\nu_{av}' - 230$ (cm$^{-1}$). From the $\nu_{av}'$ for [Co(NO)$_2$diphos][PF$_6$] of 1749 cm$^{-1}$ we predict that the average value of the Co–N–O angle is 174°, in excellent agreement with the observed value of 174.4 (14)°.

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# A Linear $RN_2$–Transition Metal Linkage. The Structure of $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3 \cdot 3C_6H_6$

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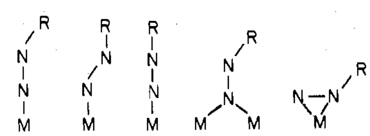
The structure of $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3 \cdot 3C_6H_6$ has been determined crystallographically and consists of discrete molecules of the diazo complex and solvent. The complex crystallizes from benzene–methanol in the triclinic space group $C_i^1$-$P\bar{1}$ with two formula units in a unit cell of dimensions $a$ = 23.80 (1) Å, $b$ = 12.683 (6) Å, $c$ = 12.793 (6) Å, $\alpha$ = 105.63 (2)°, $\beta$ = 99.16 (2)°, $\gamma$ = 101.00 (3)°, $\rho_{exptl}$ = 1.25 (3) g/cm$^3$, and $\rho_{calcd}$ = 1.242 g/cm$^3$. The structure was solved by Patterson methods. Least-squares refinement has led to a final value of the conventional $R$ index for $F_o > 3\sigma(F_o)$ of 0.072 based on 5590 reflections. This complex of Ru(II) possesses pseudooctahedral geometry with cis hydrido ligands and meridinal phosphine ligands. The diazo group $N_2B_{10}H_8S(CH_3)_2$ is trans to H(1): H(1)–Ru–N(1) = 173 (2)°. The RuNNB segment is essentially linear: Ru–N(1)–N(2) = 175.9 (6)° and N(1)–N(2)–B(1) = 172.7 (8)°. This is the first reported example of a transition metal–diazo complex containing the totally linear MNNR linkage. The boron cage possesses regular bicapped Archimedean antiprism geometry; the B–B distances within the square plane are 1.83–1.87 Å with B–B–B bond angles of approximately 90°. The B–B′ distances of bridging boron atoms range from 1.76 to 1.81 Å with B–B′–B angles of approximately 60°. Some important distances are Ru–N(1) = 1.889 (8), N(1)–N(2) = 1.115 (8), and N(2)–B(1) = 1.50 (1) Å.

## Introduction

Current interest in aryldiazo ligands arises not only because of their close relationship to nitrosyl and dinitrogen ligands but also because of their varied modes of bonding and their utility as intermediates in the synthesis of aryldiazene and arylhydrazine ligands.[1-9] The varied coordination geometries attainable by nitrosyl and aryldiazo ligands are indicative of their chemical versatility:



A B C D E

Structural studies have shown that the aryldiazo ligand can adopt a doubly bent geometry (B)[10,11] and a singly bent geometry (A)[12-16] and can bridge two metal atoms (D).[17] In these bonding modes the aryldiazo ligand ($RN_2^+$) is similar to the isoelectronic nitrosyl ligand; indeed, nitrosyl and aryldiazo ligands have been compared structurally in almost identical coordination environments.[14,18,19]

In the search for as yet unobserved bonding modes (e.g., C) and for intermediate geometries,[20] the use of infrared $\nu$(NN) stretching frequencies and especially of empirically corrected frequencies $\nu'$(NN)[11,14] has proved invaluable. The complex $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ (Ph = phenyl; Me = methyl), prepared by Knoth[21] by the reaction of $RuH_2(N_2)(PPh_3)_3$ with $N_2B_{10}H_8SMe_2$, shows a value of $\nu$(NN) of 2060 cm$^{-1}$ and an empirically corrected value $\nu'$(NN) of 1910 cm$^{-1}$. This complex is thus a prime candidate to be the first example of the totally linear coordination mode (C). Moreover, on the basis of our recent work on the Ni(diazofluorene)($t$-BuNC)$_2$ complex,[20,22] in which bonding mode E was observed for the first time, it appears as though the reaction chemistry and the bonding modes of neutral $RN_2$ species with transition metals will differ considerably from those of the more heavily studied $RN_2^+$ species. We have thus begun a systematic investigation of the bonding and chemistry of transition metal–$RN_2$ species. Here we report the structure of $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ which indeed does provide the first example of the totally linear bonding mode (C).

## Experimental Section

A sample of $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ was kindly supplied by Dr. W. H. Knoth. Recrystallization of the yellow powder from benzene–methanol yielded yellow, slightly air-sensitive crystals. Because the crystals slowly lose benzene of crystallization, freshly prepared crystals were mounted in capillaries in an atmosphere of the solvent in order to prevent desolvation during data collection.

Preliminary film data showed the crystals to belong to the triclinic system with no systematic absences. The centrosymmetric space group $P\bar{1}$ was shown to be the correct choice on the basis of successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices. Accurate unit cell dimensions were determined by a least-squares analysis of the angular positions of 14 hand-centered reflections in diverse regions of reciprocal space (in the range $37 \geq 2\theta \geq 30°$). See Table I for pertinent details on the crystal and data collection.

Data collection was carried out on a Picker four-circle diffractometer. Background counts were measured at both ends of the scan range with both the counter and the crystal stationary. The intensities of six standard reflections were measured every 100 reflections. The deviations of these standards were all within counting statistics. The intensities of 6759 reflections (all $-h$, $\pm k$, and $\pm l$ reflections) were measured out to $2\theta$ = 95.00° using Cu K$\alpha$ radiation. A value of $p$

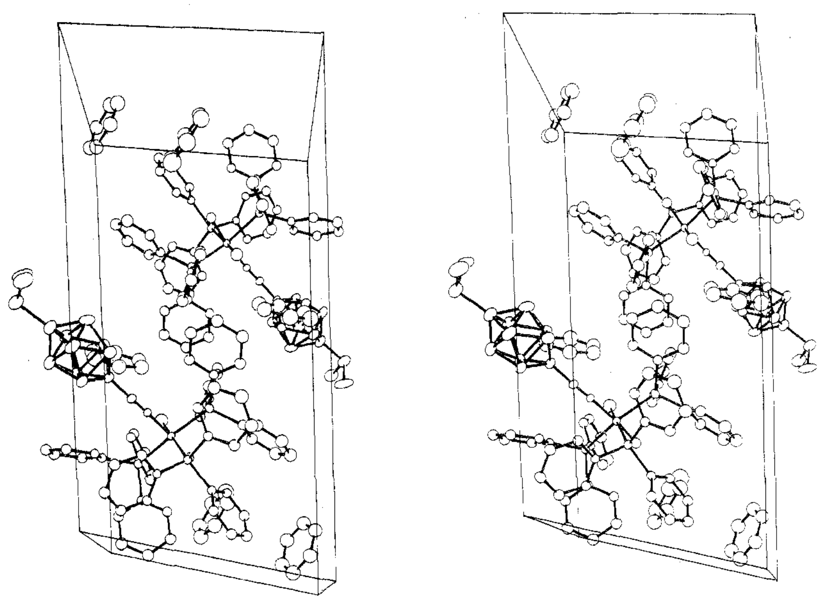


**Figure 1.** Stereoview of a unit cell of $RuH_2[N_2B_{10}H_8S(CH_3)_2][P(C_6H_5)_3]_3 \cdot 3C_6H_6$. The *x* axis is almost vertical pointing toward the bottom of the page, the *y* axis is perpendicular to the paper pointing away from the reader, and the *z* axis is horizontal to the right. Vibrational ellipsoids are drawn at the 20% probability level.

of 0.04 was used in the calculation of $\sigma(F_o^2)$.[23] Of the 6759 reflections measured, 6544 are unique and of these 5590 have $F_o^2 > 3\sigma(F_o^2)$. An absorption correction was applied to the data using Gaussian integration.[24]

The ruthenium and phosphorus atoms were located readily from a sharpened, origin-removed Patterson synthesis. Full-matrix least-squares refinements and difference Fourier synthesis assuming the centrosymmetric space group $P\bar{1}$ were used to locate all remaining atoms. Initially the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, *w*, are taken as $4F_o^2/\sigma^2(F_o^2)$. In the final two cycles of refinement, the quantity minimized was $\sum w(F_o^2 - F_c^2)^2$ and $w = 1/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum|F_o^2 - F_c^2|/\sum F_o^2$ and $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. For refinements on $|F_o|$ the agreement indices are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[25] Anomalous dispersion terms for Ru, P, and S were included in $F_c$.[26]

Each phenyl group was treated throughout the refinement as a planar rigid body with uniform C–C distances of 1.392 Å and individual isotropic thermal parameters for each carbon atom. All phenyl hydrogen atom positions were idealized; the C–H distance was assumed to be 0.95 Å with normal C–C–H bond angles. The positions of the boron hydrogen atoms and the methyl hydrogen atoms were found in a difference Fourier map and were idealized; the B–H distance was assumed to be 1.12 Å. All hydrogen atoms on the ligand were included as fixed contributions in the final anisotropic refinements. The positions and isotropic thermal parameters of the two hydrido ligands were also refined.

The final agreement indices, based on refinement of $F_o^2$ with 6544 reflections (including $F_o^2 \leq 0$) and 324 variables, are $R = 0.105$ and $R_w = 0.177$. The conventional index on $F_o$ for $F_o^2 > 3\sigma(F_o^2)$ is 0.072. An analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of $F_o^2$, setting angles, and Miller indices shows no unusual trends.

The highest peak in the final difference Fourier map of 2.6 e Å$^{-3}$ is approximately equidistant from the S, B(10), C(1), and C(2) atoms. This peak cannot be explained by us as resulting from methyl disorder nor can we make chemical sense out of it.

The final positional and thermal parameters of atoms and groups appear in Tables II and III, the idealized positions of the hydrogen atoms in Table IV,[27] and the root-mean-square amplitudes of vibration in Table V.[27] A listing of the observed and calculated structure amplitudes is available.[27]

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

| | |
|---|---|
| Compd | $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3 \cdot 3C_6H_6$ |
| Formula | $C_{74}H_{79}B_{10}N_2P_3RuS$ |
| Formula wt | 1330.63 |
| *a* | 23.80 (1) Å |
| *b* | 12.683 (6) Å |
| *c* | 12.793 (6) Å |
| α | 105.63 (2)° |
| β | 99.16 (2)° |
| γ | 101.00 (3)° |
| *V* | 3558 Å$^3$ |
| *Z* | 2 |
| Density | 1.242 (calcd), 1.25 (3) g/cm$^3$ (exptl) |
| Space group | $C_i^1$-$P\bar{1}$ |
| Crystal dimensions | 0.18 mm × 0.32 mm × 0.17 mm; 0.7 × 10$^{-2}$ mm$^3$ volume |
| Crystal shape | Prism with bounding planes $\{1\bar{1}0\}$, $\{001\}$, $\{100\}$, and $\{10\bar{1}\}$ |
| Temp | 25 °C |
| Radiation | Cu K$\alpha_1$ (λ 1.540 562 Å) |
| μ(Cu Kα) | 30.45 cm$^{-1}$ |
| Transmission factors | 0.555–0.733 |
| Receiving aperture | 5.0 mm wide × 4.0 mm high; 33 cm from the crystal |
| Takeoff angle | 3.8° |
| Scan speed | 2.0° in 2θ/min |
| Scan range | 0.9° below K$\alpha_1$ to 0.9° above K$\alpha_2$ |
| Background counting time, total | 20 s |
| 2θ limits | 2.8°–95.0° |
| Final no. of variables | 324 |
| Unique data used | 6544; for $F_o^2 > 3\sigma(F_o^2)$, 5590 |
| Error in observation of unit wt | 2.63 e$^2$ |
| *R* | 0.105 (on $F_o^2$); 0.072 (on $F_o$ for $F_o > 3\sigma(F_o)$) |
| $R_w$ | 0.177 (on $F_o^2$) |

## Discussion

The crystal structure of $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3 \cdot 3C_6H_6$ consists of the packing of two molecules of the ruthenium complex and six benzene molecules in the unit cell, Å, shown in the stereodrawing (Figure 1). There are no significant intermolecular interactions between molecules of the complex, the shortest distance being 2.41 Å between H1C(15) and H1B(8). The closest contact between solvent molecules and the complex is 2.42 Å between H1C(103) and H3C(1). A perspective view of the complex together with the numbering scheme is shown in Figure 2. Phenyl rings 1, 2, and 3 are bound to atom P(1), rings 4, 5, and 6 to atom P(2), and rings 7, 8, and 9 to atom P(3), as shown in the stereo-

**Table II.** Positional and Thermal Parameters for the Nongroup Atoms of $RuH_2[N_2B_{10}H_8S(CH_3)_2][P(C_6H_5)_3]_3$

| ATOM | X[A] | Y | Z | B11[B] OR B,A$^2$ | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|---|---|---|
| RU | 0.246861(27) | 0.377015(50) | 0.226751(52) | 14.97(16) | 50.98(58) | 61.92(60) | 7.03(22) | 5.36(22) | 21.00(43) |
| P(1) | 0.325011(95) | 0.53371(18) | 0.32071(18) | 17.31(53) | 61.8(19) | 72.5(20) | 5.52(79) | 4.23(81) | 20.1(16) |
| P(2) | 0.177592(91) | 0.23122(17) | 0.24664(18) | 17.34(53) | 58.1(19) | 68.4(19) | 8.17(78) | 7.57(80) | 27.5(15) |
| P(3) | 0.191598(91) | 0.44942(17) | 0.09708(17) | 17.51(52) | 56.4(18) | 63.7(19) | 9.53(78) | 4.85(78) | 21.9(15) |
| S | 0.40563(17) | -0.16435(32) | -0.27928(33) | 44.9(11) | 170.0(41) | 187.1(43) | 38.3(17) | 27.5(18) | 16.1(34) |
| N(1) | 0.27539(27) | 0.28957(55) | 0.11212(58) | 15.5(17) | 49.6(60) | 69.9(65) | 8.6(25) | 10.5(27) | 18.5(51) |
| N(2) | 0.29155(29) | 0.23287(60) | 0.04708(62) | 17.8(18) | 71.5(69) | 77.8(70) | 14.1(29) | 7.7(29) | 21.0(59) |
| C(1) | 0.43193(69) | -0.1106(13) | -0.3762(14) | 67.1(54) | 240.(20) | 280.(20) | 55.4(85) | 95.9(91) | 123.(17) |
| C(2) | 0.47158(53) | -0.1526(14) | -0.1892(11) | 24.3(34) | 382.(24) | 163.(15) | 50.1(77) | -13.3(58) | -89.(15) |
| B(1) | 0.31822(45) | 0.15428(84) | -0.02828(83) | 23.8(28) | 72.7(95) | 70.6(93) | 20.2(42) | 10.9(41) | 29.3(79) |
| B(2) | 0.31692(49) | 0.02202(91) | -0.03088(92) | 25.4(29) | 85.(10) | 87.(10) | 14.2(44) | 10.0(44) | 26.5(84) |
| B(3) | 0.38542(49) | 0.13569(93) | 0.00029(95) | 24.3(29) | 87.(11) | 105.(11) | 14.5(45) | 14.7(46) | 34.7(90) |
| B(4) | 0.28823(50) | 0.06190(94) | -0.15228(91) | 27.8(32) | 97.(11) | 86.(10) | 27.2(49) | 8.3(46) | 26.6(89) |
| B(5) | 0.35583(54) | 0.1737(10) | -0.1226(10) | 32.6(35) | 111.(12) | 121.(13) | 24.5(53) | 28.1(54) | 70.(11) |
| B(6) | 0.31354(60) | -0.0628(11) | -0.1679(10) | 37.8(41) | 100.(13) | 105.(12) | 26.2(58) | 8.7(55) | 18.(10) |
| B(7) | 0.38259(53) | -0.0116(10) | -0.0595(10) | 33.5(33) | 112.(12) | 102.(12) | 30.4(52) | 7.3(51) | 35.(10) |
| B(8) | 0.41064(57) | 0.0909(13) | -0.1274(13) | 26.4(35) | 190.(18) | 160.(16) | 31.1(66) | 31.8(63) | 71.(14) |
| B(9) | 0.34198(66) | 0.0421(12) | -0.2328(11) | 50.8(47) | 171.(16) | 99.(12) | 54.1(73) | 36.9(63) | 58.(12) |
| B(10) | 0.37748(65) | -0.0476(12) | -0.1943(12) | 41.5(44) | 126.(15) | 135.(15) | 38.0(67) | 24.8(65) | 39.(12) |
| H(1) | 0.2151(32) | 0.4417(62) | 0.3316(61) | 5.2(20) | | | | | |
| H(2) | 0.2840(32) | 0.3328(62) | 0.3060(62) | 8.0(20) | | | | | |

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X $10^4$.

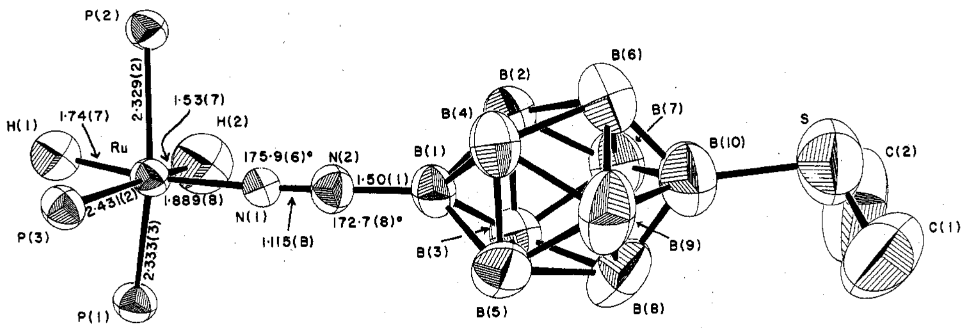



**Figure 2.** The coordination sphere with some bond distances for $RuH_2[N_2B_{10}H_8S(CH_3)_2][P(C_6H_5)_3]_3$. Vibrational ellipsoids are drawn at the 50% probability level.

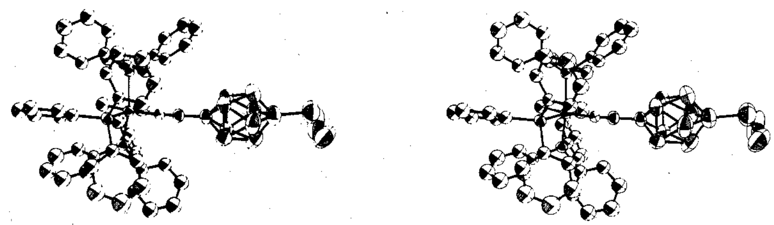


**Figure 3.** Stereoview drawing of an individual molecule of $RuH_2[N_2B_{10}H_8S(CH_3)_2][P(C_6H_5)_3]_3$. Vibrational ellipsoids are drawn at the 50% probability level. The H atoms have been omitted for the sake of clarity.

drawing of the complex (Figure 3). The complex has octahedral coordination geometry but is somewhat distorted owing to the steric interactions of the bulky phosphine ligands with the boron cage and the small bulk of the hydrido ligands. The three meridinal phosphine groups are bent away from the boron cage by differing amounts: P(3)–Ru–N(1) = 91.7 (2)°, P(2)–Ru–N(1) = 98.1 (2)°, and P(1)–Ru–N(1) = 104.7 (2)°, thus causing the P(1)–Ru–P(2) angle to decrease to 144.99 (8)° (see Table VI).

The Ru–H distances of 1.53 (7) and 1.74 (7) Å, as well as the Ru–P distances of 2.333 (3), 2.329 (3), and 2.431 (3) Å, are in the range expected for ruthenium–hydridophosphine complexes.[28-30] The Ru–P(3) distance of 2.431 Å is significantly longer than the Ru–P distances of the trans phosphine ligands. This lengthening of the M–P bond as a result of the trans influence of the hydrido ligand has been observed before in metal–hydridophosphine complexes.[30-33] A comparison of bond distances for phosphine ligands cis and trans to the hydrido ligand is given in Table VII.

**The Boron Cage.** The boron cage possesses regular bicapped Archimedean antiprism geometry; the average B–B distance within the equatorial plane is 1.84 Å with average B–B–B bond angles of 90.0°. The average apex–equatorial B–B distance is 1.65 Å with $B_e$–$B_a$–$B_e$ = 67.6° (e = equatorial; a = axial); the average B–B distance between equatorial planes B(2)–B(3)–B(4)–B(5) and B(6)–B(7)–B(8)–B(9) is 1.79 Å with an average bridging B–B–B angle of 61.8°. These values compare quite favorably with those determined by Dobrott and Lipscomb for $Cu_2B_{10}H_{10}$.[34]

The geometry about the apical boron atoms in the coor-

**Table III.** Derived Parameters for the Rigid-Group Atoms of $RuH_2[N_2B_{10}H_8S(CH_3)_2][P(C_6H_5)_3]_3$

| ATOM | X | Y | Z | B, $Å^2$ | ATOM | X | Y | Z | B, $Å^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C(11) | 0.38864(22) | 0.55886(50) | 0.25733(47) | 4.28(18) | C(71) | 0.14462(21) | 0.33347(36) | -0.02332(38) | 3.24(16) |
| C(12) | 0.40376(25) | 0.46355(37) | 0.19637(50) | 4.94(20) | C(72) | 0.16824(18) | 0.28311(45) | -0.11145(45) | 4.49(19) |
| C(13) | 0.45026(28) | 0.47585(46) | 0.14305(50) | 6.02(23) | C(73) | 0.13477(25) | 0.18544(46) | -0.19471(39) | 5.15(21) |
| C(14) | 0.48165(24) | 0.58346(57) | 0.15069(53) | 6.76(25) | C(74) | 0.07768(23) | 0.13813(38) | -0.18985(41) | 5.27(21) |
| C(15) | 0.46653(27) | 0.67877(41) | 0.21166(56) | 6.64(25) | C(75) | 0.05406(18) | 0.18850(45) | -0.10172(48) | 4.94(20) |
| C(16) | 0.42003(28) | 0.66647(40) | 0.26498(50) | 5.59(22) | C(76) | 0.08753(22) | 0.28617(43) | -0.01845(38) | 3.85(17) |
| C(21) | 0.30570(26) | 0.67003(42) | 0.35942(51) | 4.21(18) | C(81) | 0.14129(21) | 0.53730(41) | 0.13894(42) | 3.71(17) |
| C(22) | 0.30059(29) | 0.72970(54) | 0.28278(41) | 5.52(22) | C(82) | 0.09554(24) | 0.54567(45) | 0.06101(31) | 4.56(19) |
| C(23) | 0.27969(31) | 0.82706(53) | 0.30768(53) | 7.10(26) | C(83) | 0.05791(21) | 0.61322(50) | 0.09557(43) | 5.11(21) |
| C(24) | 0.26392(31) | 0.86475(47) | 0.40922(61) | 7.30(27) | C(84) | 0.06604(23) | 0.67241(46) | 0.20807(48) | 5.57(22) |
| C(25) | 0.26904(31) | 0.80507(58) | 0.48586(46) | 7.57(28) | C(85) | 0.11178(25) | 0.66404(45) | 0.28600(33) | 5.06(20) |
| C(26) | 0.28993(29) | 0.70771(54) | 0.46096(46) | 5.89(23) | C(86) | 0.14941(20) | 0.59649(46) | 0.25143(38) | 4.00(18) |
| C(31) | 0.36084(25) | 0.52921(50) | 0.45808(38) | 4.12(18) | C(91) | 0.23852(23) | 0.53496(45) | 0.03218(47) | 3.89(17) |
| C(32) | 0.32615(18) | 0.48666(52) | 0.52282(51) | 5.44(21) | C(92) | 0.28738(26) | 0.50006(42) | 0.00188(52) | 4.83(20) |
| C(33) | 0.35216(27) | 0.48373(55) | 0.62741(49) | 6.64(25) | C(93) | 0.32616(23) | 0.56685(57) | -0.03940(57) | 6.76(25) |
| C(34) | 0.41280(29) | 0.52335(59) | 0.66725(40) | 6.78(25) | C(94) | 0.31608(27) | 0.66856(54) | -0.05037(59) | 7.53(28) |
| C(35) | 0.44746(19) | 0.56590(56) | 0.60251(52) | 6.37(24) | C(95) | 0.26721(30) | 0.70346(42) | -0.02006(59) | 6.78(25) |
| C(36) | 0.42147(23) | 0.56883(51) | 0.49792(48) | 5.29(21) | C(96) | 0.22843(23) | 0.63666(49) | 0.02121(51) | 5.23(21) |
| C(41) | 0.10095(18) | 0.23831(45) | 0.22997(46) | 3.60(17) | C(101) | 0.39243(42) | 0.04983(75) | 0.29873(72) | 10.74(39) |
| C(42) | 0.08970(22) | 0.34421(37) | 0.26964(45) | 4.34(19) | C(102) | 0.41872(44) | 0.02960(67) | 0.3945(10) | 12.45(46) |
| C(43) | 0.03225(26) | 0.35628(40) | 0.25052(51) | 5.67(22) | C(103) | 0.43674(39) | 0.1165(10) | 0.49562(76) | 12.34(46) |
| C(44) | -0.01395(19) | 0.26245(55) | 0.19174(55) | 6.41(24) | C(104) | 0.42848(41) | 0.22363(81) | 0.50089(65) | 10.37(38) |
| C(45) | -0.00271(22) | 0.15656(44) | 0.15207(50) | 6.51(24) | C(105) | 0.40220(41) | 0.24386(63) | 0.40508(92) | 10.21(36) |
| C(46) | 0.05474(26) | 0.14449(35) | 0.17119(48) | 4.96(20) | C(106) | 0.38417(37) | 0.15696(93) | 0.30400(68) | 9.80(36) |
| C(51) | 0.19620(24) | 0.22124(49) | 0.38786(37) | 3.75(17) | C(111) | 0.13695(30) | -0.08235(78) | -0.42038(73) | 9.46(34) |
| C(52) | 0.16505(22) | 0.25926(52) | 0.46804(53) | 5.84(22) | C(112) | 0.12054(37) | -0.04003(66) | -0.50749(77) | 8.92(32) |
| C(53) | 0.18428(29) | 0.26121(58) | 0.57756(46) | 7.49(28) | C(113) | 0.06175(44) | -0.06733(75) | -0.56281(61) | 9.33(34) |
| C(54) | 0.23465(30) | 0.22514(59) | 0.60691(37) | 6.93(26) | C(114) | 0.01937(29) | -0.13694(80) | -0.53102(78) | 10.51(39) |
| C(55) | 0.26580(22) | 0.18712(53) | 0.52673(51) | 5.53(22) | C(115) | 0.03579(39) | -0.17926(69) | -0.44392(83) | 10.45(38) |
| C(56) | 0.24657(24) | 0.18517(49) | 0.41721(44) | 4.71(19) | C(116) | 0.09458(46) | -0.15197(75) | -0.38860(63) | 9.98(36) |
| C(61) | 0.17071(24) | 0.08840(34) | 0.15684(38) | 3.52(17) | C(121) | 0.09424(57) | -0.54037(83) | -0.29593(96) | 11.90(44) |
| C(62) | 0.16593(25) | -0.00461(47) | 0.19625(33) | 4.72(19) | C(122) | 0.06439(35) | -0.53257(86) | -0.3956(10) | 11.78(42) |
| C(63) | 0.15829(27) | -0.11243(38) | 0.12268(48) | 5.92(23) | C(123) | 0.09327(55) | -0.46659(98) | -0.45157(70) | 11.30(42) |
| C(64) | 0.15543(27) | -0.12724(34) | 0.00972(44) | 5.41(21) | C(124) | 0.15200(56) | -0.40841(83) | -0.4079(10) | 12.31(45) |
| C(65) | 0.16022(25) | -0.03423(46) | -0.02969(31) | 4.83(20) | C(125) | 0.18186(36) | -0.41622(94) | -0.3083(11) | 15.12(58) |
| C(66) | 0.16785(24) | 0.07359(38) | 0.04388(41) | 3.66(17) | C(126) | 0.15297(57) | -0.4822(10) | -0.25228(73) | 13.31(50) |

RIGID GROUP PARAMETERS

| GROUP | $X_C$ [A] | $Y_C$ | $Z_C$ | DELTA [B] | EPSILON | ETA |
|---|---|---|---|---|---|---|
| RING1 | 0.43514(18) | 0.57116(36) | 0.20401(33) | -0.1624(38) | -2.8213(36) | 2.3954(39) |
| RING2 | 0.28481(17) | 0.76739(36) | 0.38432(37) | 2.862(11) | -1.9430(38) | -2.182(11) |
| RING3 | 0.38662(18) | 0.52628(32) | 0.56266(34) | -1.2608(41) | 2.8030(36) | -2.0730(40) |
| RING4 | 0.04350(17) | 0.25038(33) | 0.21086(31) | 2.7686(36) | 2.7008(37) | -3.0913(39) |
| RING5 | 0.21543(18) | 0.22319(32) | 0.49738(34) | -2.1193(42) | 2.6918(34) | -1.6765(43) |
| RING6 | 0.16307(14) | -0.01942(31) | 0.08328(31) | -0.0291(56) | 2.2452(29) | 1.4685(55) |
| RING7 | 0.11115(16) | 0.23580(30) | -0.10658(30) | 1.5247(42) | -2.4366(31) | 0.9299(43) |
| RING8 | 0.10366(16) | 0.60485(29) | 0.17350(31) | -1.7767(64) | -2.1161(31) | -1.0334(65) |
| RING9 | 0.27740(18) | 0.60176(35) | -0.00909(33) | 0.6069(37) | -2.9141(38) | 2.5917(40) |
| RING10 | 0.41046(24) | 0.13673(57) | 0.39981(57) | 0.3609(63) | 2.7439(67) | -2.0324(61) |
| RING11 | 0.07816(28) | -0.10965(46) | -0.47570(48) | 2.8090(79) | -2.4180(53) | 2.7741(76) |
| RING12 | 0.12312(34) | -0.47439(56) | -0.35193(61) | -1.6976(90) | -2.5713(77) | 0.7973(76) |

[A] $X_C$, $Y_C$, AND $Z_C$ ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

dinated $N_2B_{10}H_8SMe_2$ ligand agrees very well with that found for $B_5H_9$ by Dulmage and Lipscomb.[35] Here the $B_a$–$B_e$ distance is 1.66 Å with $B_e$–$B_a$–$B_e$ = 64.6°. The B–B distance in the equatorial plane is 1.77 Å, with B–B–B = 90° by imposed symmetry on the molecule.

**The Diazo Ligand.** The dinitrogen portion of the diazo ligand $N_2B_{10}H_8SMe_2$ assumes the totally linear (C) geometry in this complex. The Ru–N(1)–N(2) angle (175.9 (6)°) and the N(1)–N(2)–B(1) angle (172.7 (8)°) are very nearly linear; thus both atoms N(1) and N(2) appear to possess approximate sp hybridization. Atom N(1) lies in the plane defined by Ru, H(1), H(2), P(3), and N(1); the distances of these atoms from the least-squares plane are 0.0001 (6), −0.20 (7), 0.05 (7), 0.000 (2), and −0.000 (6)Å, respectively.

Lipscomb and Reddy[36] have reported the structure of $B_{10}H_{12}(CH_3CN)_2$; the B–N–C group is linear, also indicating sp hybridization of the nitrogen atom. The B–N distance of 1.523 (7) Å for the acetonitrile compound can be compared with the N(2)–B(1) distance of 1.50 (1) Å for the $N_2B_{10}H_8SMe_2$-coordinated ligand.

The most striking feature of the metrical details of the diazo ligand in this ruthenium complex is the unusually long Ru–N(1) bond length of 1.889 (8) Å. This distance is significantly longer (~0.1 Å) than comparable distances in Ru and Os aryldiazo and nitrosyl complexes.[13,14,37–39] Only $OsH(CO)(NNPh)(PPh_3)_2$ and $[Os(CO)_2(NO)(PPh_3)_2][ClO_4]$

**Table VI.** Selected Distances (Å) and Angles (deg) in $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3\cdot 3C_6H_6$

Bond Distances

| | | | | | |
|---|---|---|---|---|---|
| Ru-P(1) | 2.333 (3) | | B(1)-B(2) | 1.66 (1) | |
| Ru-P(2) | 2.329 (2) | | B(1)-B(3) | 1.66 (1) | |
| Ru-P(3) | 2.431 (2) | | B(1)-B(4) | 1.65 (1) | |
| Ru-N(1) | 1.889 (8) | | B(1)-B(5) | 1.65 (1) | $B_e$-$B_a$ = 1.65 (3) |
| Ru-H(1) | 1.74 (7) | | B(6)-B(10) | 1.60 (2) | |
| Ru-H(2) | 1.53 (7) | | B(7)-B(10) | 1.64 (2) | |
| P(1)-C(11) | 1.843 (6) | | B(8)-B(10) | 1.70 (2) | |
| P(1)-C(21) | 1.833 (6) | | B(9)-B(10) | 1.67 (2) | |
| P(1)-C(31) | 1.848 (6) | | B(2)-B(3) | 1.87 (1) | |
| P(2)-C(41) | 1.825 (5) | | B(2)-B(4) | 1.83 (1) | |
| P(2)-C(51) | 1.834 (6) | P-C = 1.836 (10)[a] | B(3)-B(5) | 1.84 (2) | |
| P(2)-C(61) | 1.826 (5) | | B(4)-B(5) | 1.84 (2) | $B_e$-$B_e$ = 1.84 (1) |
| P(3)-C(71) | 1.841 (4) | | B(6)-B(7) | 1.85 (2) | |
| P(3)-C(81) | 1.831 (6) | | B(6)-B(9) | 1.83 (2) | |
| P(3)-C(91) | 1.852 (7) | | B(7)-B(8) | 1.83 (2) | |
| N(1)-N(2) | 1.115 (8) | | B(8)-B(9) | 1.83 (2) | |
| N(2)-B(1) | 1.50 (1) | | B(2)-B(6) | 1.77 (2) | |
| B(10)-S | 1.89 (1) | | B(2)-B(7) | 1.76 (2) | |
| S-C(1) | 1.71 (1) | | B(3)-B(7) | 1.80 (2) | bridging $B_e$-$B_e$ = 1.79 (2) |
| S-C(2) | 1.75 (1) | | B(4)-B(6) | 1.77 (2) | |
| | | | B(4)-B(9) | 1.78 (2) | |
| | | | B(5)-B(8) | 1.82 (2) | |
| | | | B(5)-B(9) | 1.80 (2) | |

Bond Angles

| | | | | |
|---|---|---|---|---|
| P(1)-Ru-P(2) | 144.99 (8) | B(2)-B(1)-B(3) | 68.4 (6) | |
| P(1)-Ru-P(3) | 101.27 (8) | B(2)-B(1)-B(4) | 67.1 (7) | |
| P(2)-Ru-P(3) | 104.30 (8) | B(3)-B(1)-B(5) | 67.5 (7) | |
| P(1)-Ru-N(1) | 104.7 (2) | B(4)-B(1)-B(5) | 67.7 (7) | $B_e$-$B_a$-$B_e$ = 67.5 (12) |
| P(2)-Ru-N(1) | 98.1 (2) | B(6)-B(10)-B(7) | 69.7 (8) | |
| P(3)-Ru-N(1) | 91.7 (2) | B(6)-B(10)-B(9) | 68.1 (8) | |
| Ru-N(1)-N(2) | 175.9 (6) | B(7)-B(10)-B(8) | 66.5 (8) | |
| N(1)-N(2)-B(1) | 172.7 (8) | B(8)-B(10)-B(9) | 65.7 (8) | |
| N(2)-B(1)-B(4) | 129.5 (8) | B(2)-B(1)-B(5) | 103.8 (8) | |
| N(2)-B(1)-B(5) | 131.0 (8) | B(3)-B(1)-B(4) | 104.0 (8) | |
| N(2)-B(1)-B(3) | 126.4 (8) | B(6)-B(10)-B(8) | 104.1 (9) | |
| N(2)-B(1)-B(2) | 125.2 (8) | B(7)-B(10)-B(9) | 102.9 (9) | |
| Ru-P(1)-C(11) | 118.76 (18) | B(6)-B(2)-B(7) | 63.1 (7) | |
| Ru-P(1)-C(21) | 115.69 (20) | B(7)-B(3)-B(8) | 60.8 (7) | |
| Ru-P(1)-C(31) | 112.87 (21) | B(6)-B(4)-B(9) | 62.1 (7) | |
| Ru-P(2)-C(41) | 119.25 (23) | B(8)-B(5)-B(9) | 60.5 (7) | bridging $B_e$-$B_e$-$B_e$ = 61.9 (10) |
| Ru-P(2)-C(51) | 109.76 (18) | B(2)-B(6)-B(4) | 62.2 (6) | |
| Ru-P(2)-C(61) | 117.40 (21) | B(2)-B(7)-B(3) | 63.1 (6) | |
| Ru-P(3)-C(71) | 111.06 (19) | B(3)-B(8)-B(5) | 60.7 (7) | |
| Ru-P(3)-C(81) | 112.01 (21) | B(4)-B(9)-B(5) | 61.8 (6) | |
| Ru-P(3)-C(91) | 113.45 (20) | B(3)-B(2)-B(4) | 89.6 (7) | |
| C(11)-P(1)-C(21) | 104.76 (31) | B(2)-B(3)-B(5) | 89.6 (7) | |
| C(11)-P(1)-C(31) | 101.25 (28) | B(2)-B(4)-B(5) | 90.6 (7) | |
| C(21)-P(1)-C(31) | 101.16 (29) | B(3)-B(5)-B(4) | 90.1 (7) | $B_e$-$B_e$-$B_e$ = 90.0 (5) |
| C(41)-P(2)-C(51) | 103.25 (30) | B(7)-B(6)-B(9) | 89.3 (9) | |
| C(41)-P(2)-C(61) | 101.46 (25) | B(6)-B(7)-B(8) | 89.9 (8) | |
| C(51)-P(2)-C(61) | 103.81 (28) | B(7)-B(8)-B(9) | 90.1 (9) | |
| C(71)-P(3)-C(81) | 102.80 (23) | B(6)-B(9)-B(8) | 90.6 (8) | |
| C(71)-P(3)-C(91) | 103.10 (25) | B(6)-B(10)-S | 124.9 (9) | |
| C(81)-P(3)-C(91) | 102.30 (28) | B(7)-B(10)-S | 126.3 (9) | |
| | | B(8)-B(10)-S | 130.95 (97) | |
| | | B(9)-B(10)-S | 130.7 (9) | |
| | | B(10)-S-C(1) | 104.2 (7) | |
| | | B(10)-S-C(2) | 101.4 (6) | |
| | | C(1)-S-C(2) | 100.3 (8) | |

[a] The figure in parentheses following an average value is the larger of that estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population.

**Table VII.** Comparison of Bond Distances (Å) for Phosphine Ligands Cis and Trans to a Hydrido Ligand[a]

| Compd | M-P(trans to H) | M-P(cis to H) | Δ(trans − cis) |
|---|---|---|---|
| $IrH(CO)_2(PPh_3)_2$[b] | 2.377 (2) | 2.375 (2) | 0.002 (3) |
| $RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)$[c] | 2.333 (3) | 2.291 (16) (av) | 0.032 (2) |
| $OsH_4[P(C_2H_5)_2Ph]_3$[d] | 2.339 | 2.296 (av) | 0.143 |
| $OsHBr(CO)(PPh_3)_3$[e] | 2.56 | 2.34 | 0.22 |
| $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$[f] | 2.431 (2) | 2.331 (4) (av) | 0.100 (4) |

[a] Abbreviations: Ph, $C_6H_5$; Me, $CH_3$. [b] Reference 31. [c] Reference 30. [d] Reference 32. [e] Reference 33. [f] This work.

have comparable M-N(1) distances.[13,39] However, when the title complex is compared with the dinitrogen complex of ruthenium, $[Ru(N_3)(N_2)(en)_2][PF_6]$[40] (en = ethylenediamine), the Ru-N(1) distances are virtually identical. This similarity is also reflected in the N(1)-N(2) distances and the NN vibrational frequencies; the N(1)-N(2) distance of 1.115 (8)

**Table VIII.** Some Bond Distances and Angles for Aryldiazo Ligands and Dinitrogen Ligands[a]

| Compd | M-N(1) | N(1)-N(2) | N(2)-X | M-N-N | N-N-X | ν(NN) (ν')[b] |
|---|---|---|---|---|---|---|
| | | M-N-N-Ar | | | | |
| $OsH(CO)(NNPh)(PPh_3)_2$[c] | 1.867 (6) | 1.211 (8) | 1.460 (10) | 171.1 (6) | 118.5 (7) | 1543 (1563) |
| $RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2$[d] | 1.784 (5) | 1.158 (6) | 1.376 (6) | 171.9 (5) | 137.1 (5) | 1881 (1851)[t] |
| $ReCl_2(NNPh)(PPhMe_2)_3$[e] | 1.77 (2) | 1.23 (2) | 1.43 (2) | 173 (2) | 119 (2) | ~1535 (1585)[u] |
| $Mo(HBPz_3)(CO)_2(NNPh)$[f] | 1.825 (4) | 1.211 (6) | 1.43 (2) | 174.2 (1) | 121.2 (2) | ~1590 (1660)[v] |
| $[Fe(CO)_2(NNPh)(PPh_3)_2][BF_4]$[g] | 1.702 (6) | 1.201 (7) | 1.404 (8) | 179.2 (5) | 124.2 (6) | 1723 (1593)[w] |
| $[RhCl(NNPh)(ppp)][PF_6]$[h] | 1.954 (8) | 1.17 (2) | 1.43 (1) | 125 (1) | 119 (1) | 1603 (1513) |
| $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$[i] | 1.835 (8) | 1.241 (11) | 1.421 (11) | 155.2 (7) | 118.8 (8) | 1619 (1559) |
| $N_2Ph^+$[j] | | 1.10 | | | | 2285 |
| | | M-N-N | | | | |
| $[Ru(N_3)(N_2)(en)_2][PF_6]$[k] | 1.894 (9) | 1.106 (11) | | 179.3 (9) | | 2103 |
| $[Rh(NH_3)_5(N_2)]Cl_2$[l] | 2.10 (1) | 1.12 (8) | | Linear | | 2105 |
| $Mo(N_2)_2(Ph_2PC_2H_4PPh_2)_2$[m] | 2.01 (1) | 1.10 (2) | | 171.8 (11) | | 2020, 1970 |
| $ReCl(N_2)(PPhMe_2)_4$[n] | 1.97 (2) | 1.06 (3) | | 177 (1) | | 1922 |
| $N_2$[j] | | 1.10 | | | | 2330 |
| | | M-N-N-X | | | | |
| $[(NH_3)_5RuN_2Ru(NH_3)_5][BF_4]_4$[o] | 1.928 (6) | 1.12 (2) | | 178.3 (5) | | 2100 |
| $MoCl_4\{N_2ReCl(PPhMe_2)_4\}_2$[p] | 1.75 (4) (Re) | 1.28 (5) | 1.99 (4) (Mo) | Linear | | 1800 |
| $(PPhMe_2)_4ClReN_2MoCl_4(OCH_3)$[q] | 1.79 (Re) | 1.21 | 1.89 (Mo) | Linear | | 1660 |
| $\{Ni[P(C_6H_{11})_3]_2\}N_2$[r] | 1.77 | 1.12 | 1.79 | 178.2 | 178.3 | 2028 |
| $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$[s] | 1.889 (8) | 1.115 (8) | 1.50 (1) | 175.9 (6) | 272.7 (8) | 2060 (1910) |

[a] Distances given in angstroms; angles given as degrees. Abbreviations: Ph, $C_6H_5$; Me, $CH_3$; Pz, $C_3H_3N_2$; en, $NH_2CH_2CH_2NH_2$; ppp, $PhP(CH_2CH_2CH_2PPh_2)_2$. [b] Frequency given in wavenumbers ($cm^{-1}$) for the phenyldiazo and dinitrogen complexes; see ref 11 and 14 for explanation of ν'. [c] Reference 13. [d] Reference 14. [e] Reference 40. [f] References 6, 7, 12. [g] Reference 15. [h] Reference 11. [i] Reference 42. [j] C. Romming and T. Tjornhom, *Acta Chem. Scand.*, **22**, 2934 (1968); C. Romming, *ibid.*, **17**, 1444 (1963); P. G. Wilkinson, *Astrophys. J.*, **126**, 1 (1957). [k] Reference 40. [l] Reference 47. [m] Reference 50. [n] Reference 51. [o] Reference 43. [p] Reference 44. [q] Reference 45. [r] Reference 46. [s] This work. [t] Reference 4. [u] This is the approximate value for the bis(phosphine)–ammine complex $ReCl_2(NH_3)(NNPh)(PPhMe_2)$. [v] This is only approximate owing to resonance coupling with phenyl vibrational modes; see ref 6 and 7. [w] References 6 and 7.

Å is the shortest such distance reported for a coordinated diazo ligand, and the $\nu_{NN}$ value of 2060 (ν' 1910 $cm^{-1}$) is the highest yet observed. Coordinated aryldiazonium ions possess N–N bond distances ranging from 1.17 to 1.24 Å and exhibit ν' values ranging from 1511 to 1851 $cm^{-1}$.[6,7,11-15,41,42] With either terminal or linearly bridging dinitrogen groups, coordinated dinitrogen complexes exhibit N–N bond distances from 1.06 to 1.28 Å and NN stretching frequencies from 1922 to 2155 $cm^{-1}$ (Table VIII).[43-51] Thus the N–N bond distance and stretching frequency of $RuH_2(N_2B_{10}H_8SMe_2)[P(C_6H_5)_3]_3$ fall within the range observed for coordinated dinitrogen complexes. If the diazo ligand is described as a two-electron donor, then the title complex formally represents a neutral diazo complex of Ru(II); more specifically the diazo ligand can be described as dinitrogen bridging ruthenium and the boron cage.

In earlier publications,[21,52] the diazo ligand $N_2B_{10}H_8SMe_2$ has been described as an "inner diazonium salt" analogous to $^+N_2B_{10}{}^{2-}H_8N_2{}^+$. The known chemistry of $B_{10}H_{10}{}^{2-}$ resembles that of a highly activated organic aromatic species[21] and its substitution derivatives form strongly electron-donating ligands. Knoth has suggested the transmission of electronic effects via apical–apical conjugation in certain $B_{10}H_{10}{}^{2-}$ derivatives.[21]

From a simplistic viewpoint, binding of the neutral $N_2B_{10}H_8SMe_2$ to a transition metal removes electron density from the nitrogen bonding orbitals through σ donation to the metal. This reduces the NN bond order, as does any π back-donation from the metal to the nitrogen π* orbitals; thus the integrity of the nitrogen triple bond could be easily lost. The $B_{10}H_{10}{}^{2-}$ group, as a σ-electron donor, could replenish electron density to the N–N bond and thus maintain the integrity of the triple bond. In analogous reactions using phenyldiazonium salts, the phenyl group acts as an electron acceptor and thus further destabilizes the NN triple bond. This is reflected in the NN distances and vibrational frequencies of bound phenyldiazo ligands as shown in Table VIII.

The halogenated analogues $1,10\text{-}B_{10}X_8(N_2)_2$ (X = Cl, Br) and their substituted derivatives have also been prepared;[52] further spectroscopic and structural studies on the effects of halogen substituents on the coordination geometry of the bound diazo ligand would help elucidate the nature of metal–nitrogen bonding and the reactions of ligands containing nitrogen–nitrogen multiple bonds.

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**Registry No.** $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3 \cdot 3C_6H_6$, 64364-98-3.

**Supplementary Material Available:** Table IV, the idealized positions of hydrogen atoms, Table V, root-mean-square amplitudes of vibration, and a listing of the observed and calculated structure amplitudes (48 pages). Ordering information is given on any current masthead page.

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# Molecular Structures of Methyl-5,10,15,20-tetraphenylporphinatothallium(III) and Chloro-5,10,15,20-tetraphenylporphinatothallium(III)

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Methyl-5,10,15,20-tetraphenylporphinatothallium(III), $CH_3TlTPP$, and methyl-2,3,7,8,12,13,17,18-octaethylporphinatothallium(III), $CH_3TlOEP$, are obtained by the reaction of diacetatomethylthallium(III) with $TPPH_2$ and $OEPH_2$, respectively. The molecule $CH_3TlTPP$ displays a square-pyramidal coordination geometry for the thallium atom and crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.046$ (2), $b = 16.244$ (3), $c = 23.373$ (5) Å, $\beta = 115.5$ (1)°, and $Z = 4$. The compound previously assumed to be aquohydroxy-5,10,15,20-tetraphenylporphinatothallium(III), $(H_2O)\cdot OHTlTPP$ is isomorphous with $CH_3TlTPP$ and is shown by x-ray analysis to be chloro-5,10,15,20-tetraphenylporphinatothallium(III), ClTlTPP, $a = 10.064$ (2), $b = 16.177$ (2), $c = 23.354$ (5) Å, and $\beta = 115.3$ (1)°. Measurement of diffracted intensities employed $\theta$–$2\theta$ scans with graphite-monochromated Mo K$\alpha$ radiation on a four-circle diffractometer. The structures were solved using the heavy-atom technique. Full-matrix least-squares refinement gave a final value of 0.045 (0.046) [for $CH_3TlTPP$(ClTlTPP)] for the conventional unweighted residual, $R$, for 2751 (2782) unique reflections having $I \geq 3\sigma(I)$. In these isomorphous complexes there are significant differences in coordination geometry, notably the displacement of the thallium atom from the porphyrin mean plane. $CH_3TlTPP$: $C_t$···Tl, 0.979; Tl–N, 2.29 (1); Tl–C, 2.147 (12) Å. ClTlTPP: $C_t$···Tl, 0.737; Tl–N, 2.21 (1); Tl–Cl, 2.420 (4) Å. The $^{13}C$ and $^1H$ NMR spectra of $CH_3TlTPP$ and $CH_3TlOEP$ show marked differences in the $^{205}Tl$–$^{13}C$ and $^{205}Tl$–$^1H$ coupling constants when compared with their chlorothallium porphyrin analogues, ClTlTPP and ClTlOEP.

The interpretation of NMR parameters of complexes containing heavy metals is of considerable current interest.[1] A knowledge of molecular structures in solution is a prerequisite for any detailed analysis of the factors influencing these parameters. For example, it has been established[2–4] that the coupling constants of several heavy-metal organometallic derivatives are dependent on solvent–complex interactions. As an extension of a program to establish the nature of these solvent interactions in organothallium complexes,[3,4] coordination environments have been sought which either preclude coordination of solvent molecules or allow exchange of solvent at a single site only. Alkylthallium porphyrins were selected