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THE STRUCTURE OF DICHLOROBIS(PHENYLAMINE)(BICYCLO[2.2.1]-HEPTA-2,5-DIENE)RUTHENIUM: A π-BONDED NORBORNADIENE COMPLEX OF RUTHENIUM(II)

JEAN-MARIE MANOLI*, ARTHUR P. GAUGHAN, Jr. and JAMES A. IBERS
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

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Summary

The structure of dichlorobis(aniline)(norbornadiene)ruthenium (aniline = phenylamine, norbornadiene = bicyclo[2.2.1] hepta-2,5-diene), $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$, has been determined from three-dimensional X-ray data collected by counter techniques and refined by a least-squares procedure to a conventional agreement index of 0.025. The complex crystallizes in space group C_{2v}^{12}–$Cmc2_1$ of the orthorhombic system in a cell of dimensions a 17.162(4), b 12.589(3), c 8.522(2) Å, V 1841.3 Å^3 with Z 4. Observed and calculated densities are 1.61(1) and 1.62 g/cm^3. The coordination geometry about the ruthenium atom is distorted octahedral with the norbornadiene moiety bound through the two double bonds. The complex possesses crystallographically imposed $C_s(m)$ symmetry with the *trans*-chloro ligands, the ruthenium atom, and the three sp^3 carbon atoms of the diolefin constrained to the mirror plane. The coordination sphere is completed by *cis*-aniline groups. Bond distances of interest are: Ru—Ct (where Ct is the center of the olefinic bond), 2.066(4); Ru—N, 2.213(3); Ru—Cl, 2.415(2) and 2.407(1) Å. The C—C distance of the olefinic bond is 1.386(6) Å, compared with 1.35 Å in the free ligand. The remaining distances in the bicyclic ligand are very close to the expected value for C—C single bonds, 1.54 Å. The Ct—Ru—Ct angle is 70.0° and the Cl—Ru—Cl angle is 156.5(5)°.

Introduction

A survey of the recent literature indicates that complexes of ruthenium have been less extensively studied than those of its second-row Group VIII counterparts, rhodium and palladium. Some current interest in ruthenium chemistry arises from the employment of certain Ru complexes as catalysts in

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* On leave from Université Paris VI, France.

the hydrogenation of olefins. Abel et al. [1] have reported the formation of metal—olefin complexes based on the bicyclic diolefin norbornadiene(bicyclo[2.2.1]hepta-2,5-diene), C_7H_8, abbreviated herein as NBD. These authors have synthesized $RuCl_2$(NBD), whose presumed polymeric structure involves chloro bridges. The amine *p*-toluidine causes fission of the chloro bridges to give a complex formulated as dichlorobis(*p*-toluidine)norbornadieneruthenium. More recently, Potvin and Pannetier [2] have studied the fission of the halogen bridges with various amines, and a series of complexes, $RuX_2(NBD)L_2$ (L = amine, X = halogen), has been prepared. Similar complexes have also been obtained with another potentially chelating diolefin, 1,5-cyclooctadiene (COD). Some hydrido complexes, e.g., $RuHX(COD)L_2$ and $RuHX(NBD)L_2$, also may be derived from these olefinic complexes. Relatively few crystal structure investigations of NBD complexes have been reported; $PdCl_2$(NBD) [3] is the only complex whose structure is related to that proposed for $RuX_2(NBD)L_2$. Consequently, to add to our information on the binding of olefins to transition metals and to aid in the interpretation of the IR and NMR spectra of these complexes we have carried out a structural investigation of a complex of the type $RuX_2(NBD)L_2$ with L = aniline and X = chloro. The results of that study are reported here.

Experimental

Crystals of $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$ suitable for X-ray analysis were grown by slow evaporation of a solution of $RuCl_2$(NBD) in aniline. Further details of the preparation and spectral properties of this and related complexes will be reported at a later date [2]. A series of precession and Weissenberg photographs employing Cu-K_α radiation show Laue symmetry *mmm* indicating that the crystals belong to the orthorhombic system. The systematic absences hkl, $h + k \neq 2n$ and $h0l$, $l \neq 2n$ are consistent with either the centrosymmetric space group D_{2h}^{17}—*Cmcm* or the noncentrosymmetric pair C_{2v}^{12}—*Cmc*2₁ and C_{2v}^{16}—*C*2*cm*. The crystals give a positive piezoelectric effect and hence must belong to one of the noncentrosymmetric space groups.

Lattice parameters at 22° were determined from a least-squares refinement [4] of the setting angles of sixteen hand-centered reflections in the range $50° \leqslant 2\theta \leqslant 60°$. All measurements were made using a Picker FACS-1 diffractometer with Ni-filtered Cu-K_{α_1} radiation (λ 1.54056 Å). The cell constants are: *a* 17.162(4), *b* 12.589(3), *c* 8.522(2) Å. The calculated density, 1.62 g/cm³, based on four formula units of $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$ in the unit cell, agrees well with a value of 1.61(1) g/cm³ measured by flotation in a methyl iodide/carbon tetrachloride mixture. With Z 4, the complex has imposed C_2 or C_s symmetry.

The crystal selected for data collection exhibited a prismatic habit with bounding faces of the forms {110} and {111} with approximate dimensions 0.23 × 0.21 × 0.65 mm along the principal crystallographic directions. In order to minimize multiple diffraction effects [5] the crystal was mounted with the [001] direction misset by approximately 5° from the diffractometer spindle axis. A total of 2974 reflections was collected by the $\theta - 2\theta$ scan technique employing both the bisecting and parallel modes of diffractometer operation.

TABLE 1

DETAILS OF DATA COLLECTION FOR $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$

Radiation	Cu-K_{α_1}, $\lambda = 1.54056$ Å
Filter	1 mil Ni foil prefilter
Take-off angle	3.25°
Scan rate	2° /min
Background times	10 sec. at scan limits
Receiving aperture	5.0 × 4.0 mm, 32 cm from crystal
Attenuators	Cu foil, ratio = 2.3; inserted at 7000 cps
Scan range	bisecting mode: $-0.9°$ (K_{α_1}) to $+0.8°$ (K_{α_2}) parallel mode: $-1.5°$ (K_{α_1}) to $+1.2°$ (K_{α_2})
Data collection limits	bisecting mode: $3° \leqslant 2\theta \leqslant 127°$ parallel mode: $120° \leqslant 2\theta \leqslant 160°$
Standards	bisecting mode: 6 every 100 reflections, all within 3σ parallel mode: 3 every 100 reflections, all within 3σ

Pertinent data collection details are given in Table 1. Throughout the entire range in 2θ, the reflections hkl and $\bar{h}\bar{k}\bar{l}$ were collected in order to facilitate the determination of the absolute configuration. In addition, all eight members of the form $\{hkl\}$ were collected in the range $3° \leqslant 2\theta \leqslant 60°$.

The data were processed in a manner previously described [4, 6] to yield values of F_o^2 and $\sigma(F_o^2)$ where $|F_o|$ is the observed structure amplitude. A value of 0.04 for p was used in the estimation of $\sigma(F_o^2)$. Of the 2974 data, 2642 were observed $[F_o^2 > 3\sigma(F_o^2)]$. An absorption correction was applied*, based on a linear absorption coefficient of 98.2 cm^{-1}. The transmission factors ranged from 0.10 to 0.32.

The members of $\{hkl\}$ which remain equivalent when Friedel's Law fails differ depending upon the aspect of the space group [7]. Accordingly, the compete data for $2\theta \leqslant 60°$ were averaged under the assumption (1) that the aspect is $mm2$ (data split into two groups depending upon the sign of l) and (2) that the aspect is $2mm$ (data split into two groups depending upon the sign of h). The corresponding R-factors for averaging were 0.021 and 0.045, respectively, providing clear proof that the aspect is $mm2$ and the space group is C_{2v}^{12}—$Cmc2_1$.

Solution and refinement of the structure

The structure was solved by standard heavy-atom techniques. Trial positions for the Ru and two Cl atoms were derived from an analysis of a three-dimensional origin-removed Patterson function. The Ru and the two Cl atoms were found to lie on the mirror plane in $Cmc2_1$ and hence symmetry m is imposed on the molecule. The remaining carbon and nitrogen atoms were located by the usual combination of Fourier and least-squares techniques although some difficulty was encountered in the early stages because of pseudosymmetry. The trial structure was refined (on F) by a full-matrix least-squares procedure.

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* In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error-function program, and Dewar's FAME normalized structure-factor program. Our full-matrix least-squares program, NUCLS, in its non-group form, closely resembles the Busing—Levy ORFLS program. Our absorption program, AGNOST, incorporates the Coppens—Leiserowitz—Rabinovich logic for Gaussian integration.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $RuCl_2(C_9H_8)(C_6H_5NH_2)_2$

Atom	x	y	z	$10^4\beta_{11}$[a] or $B(Å^2)$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru	0	0.19990(2)[b]	1/4	18.4(1)	36.9(2)	84.1(6)	0	0	1.0(2)
Cl(1)	0	0.3238(1)	0.0335(2)	39.2(5)	59.2(8)	139(2)	0	0	30(1)
Cl(2)	0	0.0285(1)	0.3752(1)	29.1(4)	52.2(7)	152(2)	0	0	36(1)
N	0.0941(1)	0.1289(2)	0.1067(3)	23(1)	61(2)	108(5)	0.2(11)	−2(1)	−12(2)
C(1)	0.1689(1)	0.1130(2)	0.1814(4)	20(1)	53(2)	104(5)	3(1)	7(1)	−15(3)
C(2)	0.2231(2)	0.1951(2)	0.1841(6)	28(1)	60(2)	135(8)	−3(1)	8(2)	−11(3)
C(3)	0.2930(2)	0.1796(3)	0.2629(11)	23(1)	99(2)	175(10)	−3(1)	−1(4)	−28(7)
C(4)	0.3090(2)	0.0875(4)	0.3369(6)	25(1)	130(4)	162(9)	11(1)	−1(3)	−2(5)
C(5)	0.2559(2)	0.0040(4)	0.3320(7)	34(1)	93(3)	201(9)	23(2)	16(3)	34(4)
C(6)	0.1853(1)	0.0171(2)	0.2531(7)	26(1)	59(2)	192(7)	7(1)	20(3)	18(5)
C(7)	0	0.2570(5)	0.5672(8)	35(2)	79(5)	109(11)	0	0	−10(5)
C(8)	0	0.3770(6)	0.5838(10)	35(2)	93(5)	196(14)	0	0	−68(8)
C(9)	0	0.3966(5)	0.4065(9)	31(2)	62(4)	189(14)	0	0	−42(6)
C(10)	0.0689(2)	0.3261(3)	0.3567(5)	27(1)	54(2)	135(8)	−4(1)	−2(2)	−25(3)
C(11)	0.0692(2)	0.2891(3)	0.4561(5)	26(1)	68(2)	100(6)	−2(1)	−4(2)	−10(3)
H(7)[c]	0	0.2211(61)	0.6417(145)	4.8[d]					
H(9)	0	0.4513(62)	0.3469(105)	5.3					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. [c] The number of the hydrogen atom indicates the carbon atom to which it is attached. [d] The isotopic temperature factors of these hydrogen atoms were not refined. Each hydrogen atom has been assigned an isotropic temperature factor 1 $Å^2$ larger than that of carbon atom to which it is attached.

The function minimized is $\Sigma w(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for all non-hydrogen atoms were taken from the usual tabulation [8], while those for H were taken from the calculations of Stewart et al. [9]. Two cycles of least-squares refinement of an isotropic thermal model for the complete trial structure using the 769 observed inner reflections resulted in convergence with values of 0.063 for R_1 and 0.089 for R_2. The agreement indices R_1 and R_2 are defined as $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{1/2}$.

At this point the refinement was expanded to include an enantiomeric model (B) related to the original arbitrary choice (A) by inversion. The complete data set, consisting of 2005 unique reflections in the range $3° \leqslant 2\theta \leqslant 160°$ of which 1713 were observed, was generated by averaging those members of a given form that remain equivalent under *mm*2. The anomalous terms for Ru, Cl, N, and C, as obtained from the tabulation of Cromer and Liberman [10], were introduced, and included in F_c [11] during subsequent calculations. One cycle of refinement of each of the enantiomorphous models resulted in values of 0.070 (R_1) and 0.096 (R_2) for enantiomer (A) and 0.057 (R_1) and 0.080 (R_2) for enantiomer (B). With the two weighted agreement factors as the basis for the Hamilton Ratio Test [12, 13], and assuming only random errors in the data, the hypothesis that enantiomer (A) is the correct absolute configuration may be rejected at the 99.5% confidence level. The refinement was therefore continued on enantiomer (B).

Suitable positions for the twelve independent hydrogen atoms were determined from a difference Fourier map based on the refined positions of enantiomer (B). The C(N)—H distances ranged from 0.80 to 1.15 Å. The position of a given hydrogen atom was idealized using a C(N)—H distance of 0.95 Å and bond angles appropriate to the atom to which it is bonded. The thermal parameter for a given hydrogen atom was arbitrarily taken as 1 Å^2 higher than the atom to which it is bonded. The contributions to the calculated structure factors from the idealized hydrogen atoms were included as fixed contributions during subsequent refinement of the model. After a further cycle of refinement, inspection of the structure factors suggested that the data are affected by extinction. An additional cycle of least-squares refinement including an anisotropic model for all non-hydrogen atoms and an isotropic correction for secondary extinction lowered the discrepancy indices to 0.031 and 0.052 for R_1 and R_2, respectively, and provided the basis for an improved model for the idealized hydrogen atoms. A difference Fourier map revealed that the idealized positions for the two hydrogen atoms bonded to the tertiary carbon atoms of the NBD moiety were somewhat unrealistic, possibly because of distortion of the bond angles about these atoms. Idealized positions for the ten remaining hydrogen atoms were recomputed and a final cycle of least-squares refinement of 123 variables based on 1713 observations resulted in values of 0.025 for R_1 and 0.035 for R_2. The details of the model include a correction for secondary extinction, an anisotropic thermal model for each non-hydrogen atom, variable positional but fixed thermal parameters for the two hydrogen atoms bonded to the tertiary carbon atoms, and fixed idealized positional and thermal parameters for the ten remaining hydrogen atoms.

TABLE 3

IDEALIZED POSITIONAL COORDINATES FOR HYDROGEN ATOMS

Atom	x	y	z	B(Å^2)
H_a [a]	0.102	0.174	0.019	4.03 [b]
H_b	0.076	0.061	0.071	4.03
H(2) [c]	0.212	0.260	0.132	4.55
H(3)	0.330	0.235	0.264	5.57
H(4)	0.356	0.080	0.393	5.86
H(5)	0.267	—0.061	0.382	5.66
H(6)	0.148	—0.039	0.246	4.71
H(8)	0.045	0.403	0.634	5.52
H(10)	0.104	0.340	0.273	4.21
H(11)	0.104	0.181	0.456	4.29

[a] H_a and H_b are bonded to the nitrogen atom of the aniline. [b] A hydrogen atom was assigned a temperature factor 1 Å^2 larger than that of the atom (nitrogen or carbon) to which it is attached. [c] The number of the hydrogen atom indicates the carbon atom to which it is bonded.

The largest parameter shifts in the final cycle were less than 0.1 of their estimated standard deviations except for the positional parameters of the two hydrogen atoms which were 0.3 times their estimated standard deviations. The standard deviation of an observation of unit weight is 0.99 e^-. A final difference map shows no peak higher than 0.3 e^-/Å^3, whereas the average electron density of a carbon atom in this structure is 2.5 e^-/Å^3. The value of the isotropic extinction parameter is 7.39(1) × 10^{-3} e^{-2}. A comparison of $\Sigma w(|F_o|-|F_c|)^2$ for various classes of reflections based on Miller indices, $|F_o|$, and setting angles shows no significant dependence on any of these quantities. Of the 292 unique reflections omitted from the refinement ($F_o^2 < 3\sigma(F_o^2)$), none had $|F_o^2-F_c^2| > 3\sigma(F_o^2)$.

The parameters obtained from the final cycle of refinement are given in Tables 2 and 3 along with their estimated standard deviations as obtained from the inverse matrix. A tabulation of observed and calculated structure amplitudes

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) ALONG THE PRINCIPAL AXES

Atom	Minimum	Intermediate	Maximum
Ru	0.1661(6)	0.1715(6)	0.1766(7)
Cl(1)	0.180(2)	0.242(1)	0.257(2)
Cl(2)	0.167(1)	0.208(1)	0.265(2)
N	0.184(4)	0.193(5)	0.230(3)
C(1)	0.157(5)	0.195(4)	0.222(4)
C(2)	0.196(5)	0.208(5)	0.242(5)
C(3)	0.187(4)	0.236(7)	0.299(8)
C(4)	0.188(5)	0.244(7)	0.327(6)
C(5)	0.189(5)	0.242(5)	0.326(6)
C(6)	0.177(5)	0.210(6)	0.285(7)
C(7)	0.197(10)	0.229(7)	0.255(8)
C(8)	0.190(8)	0.231(7)	0.333(9)
C(9)	0.186(8)	0.218(7)	0.291(10)
C(10)	0.175(5)	0.207(5)	0.247(6)
C(11)	0.181(6)	0.203(5)	0.238(5)

(X 20) has been deposited*. The root-mean-square amplitudes of vibration of the fifteen atoms refined anisotropically are given in Table 4.

Description of the structure and discussion

The structure consists of discrete molecules of $RuCl_2(NBD)(C_6H_5NH_2)_2$ situated about sites of mirror symmetry in space group *Cmc2₁*. A stereoscopic view of the contents of the unit cell is presented in Fig. 1. There are significant intermolecular H···Cl contacts between two of the mirror-related amine hydrogen atoms of one molecule and one of the chlorine atoms on an adjacent molecule. The length of this intermolecular contact, H_b···Cl(2), 2.41 Å, is significantly less than the sum of the van der Waals' radii [14] for H and Cl and well within the range for an H···Cl hydrogen bond [15]. Thus the packing is dominated by a hydrogen-bonded network consisting of intermolecular H···Cl contacts resulting in helicoidal chains of $RuCl_2(NBD)(C_6H_5NH_2)_2$ turning about the 2_1 screw axes. There are no abnormally short intermolecular contacts between the chains, all distances being greater than the sum of the van der Waals' radii. A similar arrangement is found in platinum—olefin complexes with aryl [16] and allylic [17] amines.

The coordination arrangement about the Ru atom is that of a distorted octahedron with the two chloro ligands *trans* to each other and an equatorial plane consisting of the two nitrogen atoms of *cis*-aniline groups and the midpoints of the olefinic bonds of the chelating NBD ligand. The Ru atom is displaced by only 0.025 Å from the equatorial plane. This arrangement was somewhat surprising in view of our expectation of a *trans*-aniline, *cis*-halogen structure. The geometry of the inner coordination sphere is illustrated in Fig. 2 and a stereoscopic view of the entire molecule is presented in Fig. 3. A tabulation of selected interatomic distances and angles will be found in Tables 5 and 6, respectively.

The molecule possesses crystallographically imposed $C_s(m)$ symmetry with

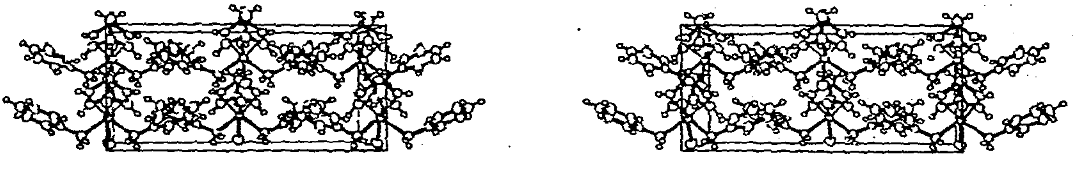

Fig. 1. A stereoscopic drawing of the unit cell of $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$. The ellipsoids for non-hydrogen atoms in this and the following drawings represent 50% probability contours of thermal motion. The thermal parameters of the hydrogen atoms have been made artificially small for the sake of clarity. The origin is at the front upper right. The horizontal axis is x and points to the left; the y axis points into the plane of the paper; the vertical axis is z and points downward.

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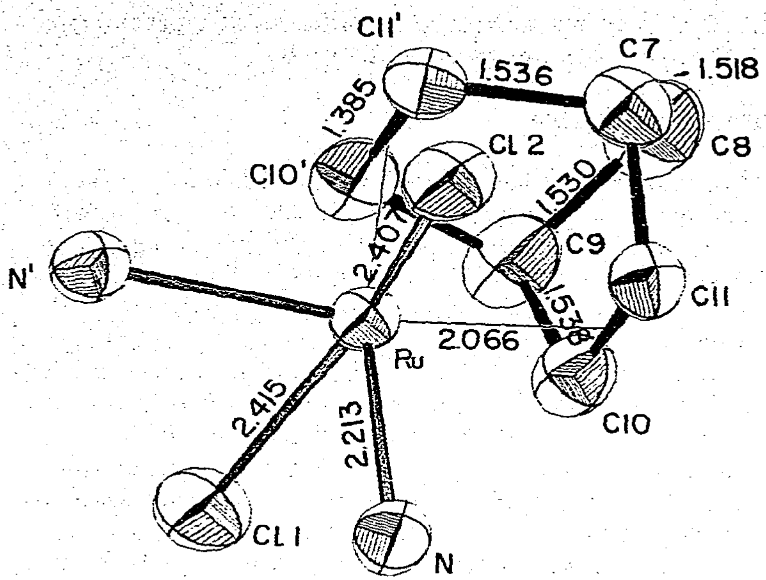


Fig. 2. A perspective view of the inner coordination sphere of $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$. Atoms C(7), C(8), C(9), Ru, Cl(1), and Cl(2) lie on the mirror plane. Atoms related by the mirror are primed. We have joined by a thin line the Ru atom and the midpoints (Ct in the tables) of the double bonds of the NBD ligand.

the mirror plane passing though the Ru and the two Cl atoms as well as C(7), C(8), and C(9) of the NBD ligand (Fig. 2). The mutually *trans*-Ru—Cl bond lengths, 2.415(2) and 2.407(1) Å are slightly longer than the Ru—Cl distances found in a number of Ru^{II} complexes [18—21] in which mutually *trans*-chloro ligands are present (2.37—2.39 Å). They are, however, slightly less than the *trans*-Ru—Cl distances of 2.446 and 2.442 Å found in the structure of $[Ru_2Cl_3\{P(C_2H_5)_2(C_6H_5)\}_6][RuCl_3\{P(C_2H_5)_2(C_6H_5)\}_3]$ [22] and a value of 2.421 Å found in $RuHCl[P(C_6H_5)_3]_3$ [23]. The Cl(1)—Ru—Cl(2) angle of 156.5(2)° is also deserving of comment. The distortion from the expected 180° appears to result from non-bonded repulsions between the two chlorine atoms and the hydrogen atoms bonded to both the tertiary [C(7) and C(9), Fig. 2] and olefinic [C(10), C(10)', C(11), C(11)', Fig. 2] carbon atoms of the NBD moiety. There are short intramolecular contacts between Cl(1) and the

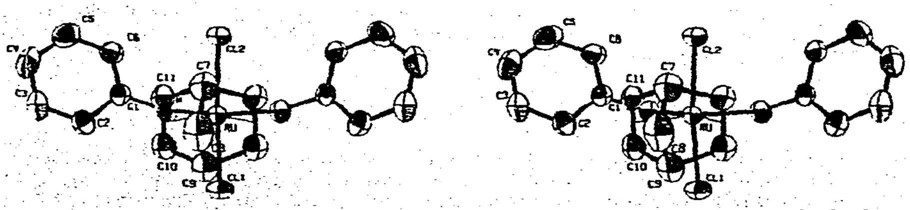


Fig. 3. A stereoscopic view of the molecule of $RuCl_2(C_7H_8)(C_6H_5NH_2)_2$. The hydrogen atoms have been omitted for clarity.

TABLE 5

SELECTED DISTANCES (Å)

Ru—Cl(1)	2.415(2)	Cl(1) ···Cl(2)	4.722(2)
Ru—Cl(2)	2.407(1)	Cl(1) ···N	3.002(8)
Ru—N	2.213(3)	Cl(2) ···N	3.073(3)
Ru—C(11)	2.177(4)	Cl(1) ···C(11)	3.939(5)
Ru—C(10)	2.181(4)	Cl(1) ···C(10)	2.998(5)
Ru—Ct ^{a}	2.066	Cl(2) ···C(11)	2.986(4)
		Cl(2) ···C(10)	3.933(4)
N—C(1)	1.447(4)	C(11) ···C(11)′	2.375(7)
		C(10) ···C(10)′	2.367(7)
C(1)—C(2)	1.390(4)	N ···C(10)	3.300(5)
C(2)—C(3)	1.389(7)	N ···C(11)	3.312(5)
C(3)—C(4)	1.349(7)	N ···N′	3.231(5)
C(4)—C(5)	1.392(6)		
C(5)—C(6)	1.395(5)	Cl(1) ···Ct	3.431
C(6)—C(1)	1.382(5)	Cl(2) ···Ct	3.423
Average	1.382(17) ^{b}	Ct ···Ct′	2.371
		N ···Ct	3.233
C(10)—C(11)	1.385(6)		
C(11)—C(7)	1.536(6)	Cl(1) ···H_a	2.58
C(10)—C(9)	1.538(5)	Cl(1) ···H(10)	2.73
C(9)—C(8)	1.530(12)		
C(7)—C(8)	1.518(9)	*Intermolecular*	
C(9)—H(9) ^{c}	0.85(8)	Cl(2) ···H_b ^{e}	2.41
C(7)—H(7)	0.78(10)	Cl(2) ···N	3.230(3)
Non-bonded distances		H(10) ···H(5) ^{f}	2.68
Intramolecular ^{d}		H(8) ···H(9)	2.69
Ru···C(7)	2.798(7)		
Ru···C(8)	3.615(7)	Cl(1) ···H(4)	2.99
Ru···C(9)	2.813(6)		

[a] The midpoint of the double bond C(10)—C(11) is labeled Ct. [b] The estimated standard deviation in parentheses is the larger of an average individual standard deviation or of the standard deviation of a single observation as calculated from the mean. [c] Recall that the positions of the hydrogen atoms H(7) and H(9) were refined. [d] Atoms related by the mirror symmetry have a prime. [e] Hydrogen-bond distances. [f] These distances are the shortest intermolecular H·····H distances.

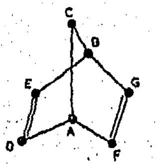
TABLE 6

SELECTED BOND ANGLES (DEG.)

Intramolecular			
Cl(1)—Ru—Cl(2)	156.5(5)	C(1)—C(5)—C(6)	119.5(3)
N—Ru—N′	93.7(1)	Average	119.9(9)
C(11)—Ru—C(11)′	66.1(2)		
C(10)—Ru—C(10)′	65.7(2)	N—C(1)—C(6)	119.7(3)
C(10)—Ru—N	97.3(1)	N—C(1)—C(2)	119.8(3)
C(11)—Ru—N	97.9(1)		
N—Ru—Cl(1)	80.7(1)	C(7)—C(8)—C(9)	93.9(5)
N—Ru—Cl(2)	83.2(1)	C(8)—C(9)—C(10)	100.3(5)
C(11)—Ru—C(10)	37.0(1)	C(10)—C(9)—C(10)′	100.5(4)
C(11)—Ru—Cl(2)	81.1(1)	C(9)—C(10)—C(11)	106.8(4)
C(10)—Ru—Cl(1)	81.2(1)	C(11)—C(7)—C(11)′	101.3(5)
		C(11)—C(7)—C(8)	101.7(4)
Ct—Ru—Ct′	70.0	C(7)—C(11)—C(10)	105.0(3)
N—Ru—Ct	98.1		
Cl(2)—Ru—Ct	99.5	H(7)—C(7)—C(11)	115(4)
Cl(1)—Ru—Ct	99.6	H(7)—C(7)—C(8)	120(8)
C(1)—N—Ru	117.4(2)	H(9)—C(9)—C(10)	107(4)
		H(9)—C(9)—C(8)	136(6)
C(6)—C(1)—C(2)	120.4(3)		
C(3)—C(2)—C(1)	118.7(3)	*Intermolecular*	
C(4)—C(3)—C(2)	121.5(4)		
C(3)—C(4)—C(5)	120.1(4)	N—H_b—Cl(2)	144.5
C(4)—C(5)—C(6)	119.5(4)		

TABLE 7

COMPARISON OF THE STRUCTURAL FEATURES OF THE COORDINATED AND UNCOORDINATED NORBORNADIENE MOLECULE



	$PdCl_2(NBD)$[a,b] (C_s) C, Ct, Ct′ in the mirror plane[c]	$Cl_2Sn(Co(CO)_2$-$NBD)_2$[d,e] G Fragment No. 1	$Cl_2Sn(Co(CO)_2$-$NBD)_2$[d,e] G Fragment No. 2	$Co_2(CO)_6(NBD)$[f] (C_1)	$RuCl_2$(NBD)-$(C_6H_5NH_2)_2$[g] (C_s) A, B, C in the mirror plane	NBD free molecule[h]
Bond distances (Å)						
E–D	1.366(9)	1.392(12)	1.418(13)	1.376(7)	1.386(6)	1.35
F–G	1.366(10)	1.388(13)	1.385(15)	1.370(8)		
A–F	1.554(5)	1.529(13)	1.548(15)	1.523(8)	1.536(6)	1.548
B–G		1.537(13)	1.569(13)	1.526(8)	1.538(5)	
A–D	1.552(5)	1.551(11)	1.561(12)	1.531(8)		
B–E		1.551(12)	1.552(12)	1.518(7)		
C–A	1.547(6)	1.565(12)	1.534(13)	1.543(9)	1.530(12)	
C–B		1.575(13)	1.566(14)	1.550(8)	1.518(9)	
Angles (deg.)						
A–C–B	94.5	93.6(6)	94.7(7)	93.4(4)	93.9(5)	97
C–B–G	99.5	100.1(8)	100.8(8)	100.0(5)	100.3(5)	97
C–A–F		99.8(7)	100.9(9)	100.4(5)	101.7(4)	
C–B–E	100.4	100.8(7)	100.9(8)	100.4(5)		
C–A–D		100.6(7)	101.0(8)	100.4(5)		
E–B–G	100.3	100.3(6)	99.0(6)	100.3(4)	100.5(4)	104
D–A–F		99.8(7)	98.7(8)	102.1(4)	101.3(5)	
B–G–F	106.9	106.4(8)	105.4(9)	107.3(5)	106.8(4)	108
G–F–A		107.7(8)	108.0(9)	106.3(5)	105.0(3)	
B–E–D	107.0	106.2(7)	105.8(8)	107.5(5)		
E–D–A		107.4(8)	106.4(8)	105.8(5)		

[a] Ref. 3. [b] The imposed symmetry of the coordinated NBD is given in parentheses. [c] Ct and Ct′ are the midpoints of the two carbon—carbon double bonds. [d] Ref. 28. [e] We have not considered the phenyl compound. [f] Ref. 27. [g] This work. [h] Ref. 29.

two symmetry-related hydrogen atoms of the aniline ligands not involved in the intermolecular hydrogen-bonding network. However, it does not appear to be possible to relate either the hydrogen-bonding arrangement or the close $H_a \cdots Cl(1)$ contacts to the Cl(1)—Ru—Cl(2) angle.

The two symmetry-related aniline groups are *cis* to each other and *trans* to the olefinic bonds of the chelating NBD ligand. The Ru—N distance, 2.213(3) Å, is rather long compared with the Ru^{II}—N distances usually found in amine complexes of ruthenium [24], 2.11—2.14 Å, suggesting that perhaps a structural *trans* effect for NBD is operative.

Recently Little and Ibers [25] summarized the Ru—N distances found in a series of porphinato—metal—amine crystal structure investigations. The long Ru^{II}—N(sp^2) distance of 2.193 Å found by these authors in the structure of Ru(TPP)(py)(CO), (TPP = tetraphenylporphinato dianion, py = pyridine), is interpreted as resulting from a *trans* influence of the carbonyl group. Similarly, March and Ferguson [26] in the structure determination of $[Ru(NH_3)_5\{(CH_3)_2SO\}][PF_6]_2$ found a Ru^{II}—N distance of 2.209 Å and attributed it to the considerable *trans* influence of the *S*-bonded dimethylsulfoxide ligand. Thus it would appear that a structural *trans* influence is responsible for the somewhat long Ru—N distance in the present complex. However, the structure determination of the square-planar complex $PdCl_2$(NBD) [3] did not reveal unusually long Pd—Cl bond lengths. Clearly, further structural work is needed to confirm the existence of a *trans* effect for coordinated norbornadiene.

The phenyl group of the aniline ligand is unremarkable, all distances and angles associated with the ring being within the range of accepted values (Tables 5 and 6). The best weighted least-squares plane through the six carbon atoms of the phenyl group is given by $7.151x - 4.309y - 7.176z - 0.574 = 0$ (orthorhombic coordinates). None of the six atoms deviates from the mean plane by more than 0.01 Å. The nitrogen atom is displaced 0.07 Å out of this plane.

The NBD ligand is bonded to the Ru atom through the carbon—carbon double bonds of the diolefin thus completing an octahedral configuration about the metal atom. The distances from the Ru atom to the olefinic carbon atoms, 2.177(4) and 2.181(4) Å, and to the centers (Ct) of the double bonds, 2.066 Å, are consistent with the corresponding distances in $PdCl_2$(NBD) [3], $Co_2(CO)_6$(NBD) [27], and $X_2Sn(Co(CO)_2(NBD))_2$, X = Cl, C_6H_5 [28]. The NBD ligand possesses imposed $C_s(m)$ symmetry with the mirror plane containing the three saturated carbon atoms and relating the two olefinic linkages. The bond distances and angles within the NBD ligand are in general conformity with the results of other structural investigations of chelating NBD ligands [3, 27, 28]. These results are collected in Table 7 together with the available structural parameters for the free NBD molecule as obtained from an electron diffraction study [29]. Reference to the table reveals that, as expected, coordination leads to a lengthening of the C—C double bonds from 1.35 Å in the free molecule to an average value of 1.38 Å in the chelate. This lengthening of the C—C double bonds upon coordination is easily accommodated within the framework of the Dewar [30], Chatt and Duncanson [31] model for the bonding of olefins to transition metals.

The major bond angle reorganizations that occur upon coordination take place at the three saturated carbon atoms while the angles at the olefinic carbon atoms are relatively unaffected. The most significant of these changes in terms of the effect of coordination are those occurring at the tertiary carbon atoms where the angles EBG and DAF decrease from a value of 104° in the free molecule to an average value of 100.3° in the coordinated species. Concurrently, the remaining angles about the tertiary carbon atoms, CBG, CAF, CBE, and CAD increase from 97° in free NBD to an average value of 100.5° in the chelate. The net result of these changes is apparently to enable the NBD ligand to approach the metal more closely by an adjustment of its bite to conform more nearly to the spatial requirements imposed by the metal orbitals. The change in the angle at the bridging carbon atom from 97° (free) to 94° (coordinated) probably reflects the cumulative effects of small changes in the distances and angles at the olefinic carbon atoms. The values do, however, serve to point up the fact that norbornadiene is considerably strained [32] and that the distortions resulting from coordination increase the strain.

As noted above, we were somewhat surprised at the stereochemical arrangement about the Ru atom in the present complex, expecting a *cis*-halogen rather than a *cis*-amine structure by analogy with the $PdCl_2$ (NBD) skeleton [3]. It remains to be established whether the present *cis*-amine structure is the exception or the rule for complexes of the general formula RuX_2(diolefin)L_2, X = halogen, L = amine. The structure of RuX_2(NBD)L_2 complexes with L = pyridine should prove enlightening in this regard.

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