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is reasonable that compared to mercapto-Mo(IV) complexes of higher coordination numbers, the Mo(IV)-S(mercapto) distance of Mo(t-BuS)$_4$ is shorter.

Since the molecular structure of tetrakis(alcoholato)molybdenum(IV) compound has not been studied by X-ray diffraction, this work contributes to our knowledge on the structural chemistry of the rather rare class of mononuclear tetracoordinate d^2 species. The electronic structure of Mo(t-BuS)$_4$, as studied by a UV photoelectron spectroscopy and X$_\alpha$-SW MO calculations, will be a subject of a separate paper.

Acknowledgment. We thank Japan Synthetic Rubber Co., Ltd., for the partial financial support and Climax Molybdenum Co. for the generous gift of molybdenum pentachloride.

Supplementary Material Available: Table listing observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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Structures, Spectroscopy, and a Mechanism of Formation of Linked-Norbornadiene Complexes of Ruthenium(II). Interaction of Ruthenium(II) with Alicyclic Hydrogen Atoms

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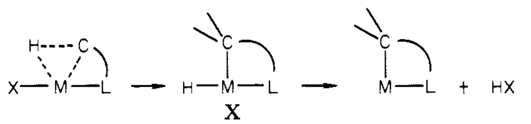
Abstract: Reduction of [RuCl$_2$(diene)]$_n$ (diene = norbornadiene (bicyclo[2.2.1]hepta-2.5-diene) or 1,5-cyclooctadiene) by means of zinc powder in the presence of norbornadiene (NBD) in refluxing acetonitrile affords a mixture of two new ruthenium(II) complexes of empirical formula RuClC$_{21}$H$_{25}$, in which three NBD molecules are involved. The structures of the cocrystallizing complexes [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)]chloro[3-(tricyclo[2.2.1.0^{2,6}]heptan-3-yl-κH^3)-*endo,endo*-bicyclo-[2.2.1]hept-5-en-2-yl-(2,5,6-η)]ruthenium(II) and [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)][*endo*-3-(bicyclo[2.2.1]hept-5-en-2-yl-κH^2)-*endo,endo*-bicyclo[2.2.1]hept-5-en-2-yl-(2,5,6-η)]chlororuthenium(II) were determined by single-crystal X-ray diffraction methods. These two isomers, differing only in the nature of the third noncoordinated NBD moiety, were found in the crystal in a ratio 86:14, respectively. Proton NMR spectroscopy of these complexes indicates a strong interaction between the ruthenium(II) atom and a hydrogen atom of the hydrocarbon ligand (δ −3.74 for the major isomer, δ −2.83 for the minor isomer), which was further substantiated by the X-ray structure determination of this complex. Relevant crystal data are as follows: space group C_i^1—$P\bar{1}$; $a = 7.389$ (2), $b = 13.271$ (4), $c = 9.439$ (3) Å; $\alpha = 105.37$ (2)°, $\beta = 101.18$ (2)°, $\gamma = 92.80$ (2)°; $V = 861.3$ Å^3 at −150 °C; $Z = 2$; $\rho_{obsd} = 1.59$ (1), $\rho_{calcd} = 1.590$ g cm^{-3}. The molecules, including hydrogen atoms, were refined on F^2, including $F_o^2 < 0$ (6762 unique data collected at −150 °C), to values for R and R_w on F^2 of 0.050 and 0.072. For the portion of data where $F_o^2 > 3\sigma(F_o^2)$ (5788 reflections), the values for R and R_w on F are 0.028 and 0.036. The primary coordination sphere is composed of one chloro, one alkyl, and three olefin ligands. Two metal–olefin bonds are provided by a free norbornadiene molecule. The third such bond is provided by a substituted norbornenyl molecule; the other olefin bond of its norbornadiene parent is now involved in (i) a metal–alkyl bond approximately trans to the chloro ligand and in (ii) a covalent bond to a nortricyclyl derivative of norbornadiene for the major component and a (second) norbornenyl derivative for the minor component. A pseudooctahedral geometry is completed by an unusually close Ru···HCR$_3$ contact of 2.10 (3) Å with the otherwise dangling nortricyclyl (or norbornenyl) component. The Ru–Cl separation is 2.483 (1) Å; the Ru–C$_{sp^3}$ separation is 2.099 (2) Å, and the six Ru–C$_{olefin}$ separations range from 2.110 (2) to 2.353 (2) Å. The C=C bond lengths (1.422 (2), 1.400 (2), and 1.385 (2) Å) are correlated with the Ru–C$_{olefin}$ separations. For the related complex [Ru(C$_{21}$H$_{25}$)(CH$_3$CN)][CF$_3$SO$_3$], generated by the reaction of RuClC$_{21}$H$_{25}$ with silver triflate in an acetonitrile solution, an even stronger interaction between the ruthenium(II) center and the hydrogen atom was inferred from the ^{1}H NMR spectrum (δ −4.93). Formation of the RuClC$_{21}$H$_{25}$ moiety from the active intermediate complex RuHCl(NBD)$_2$ by an Ru–H insertion followed by an Ru–C insertion into olefinic bonds is postulated.

Activation of carbon–hydrogen bonds by means of transition-metal complexes has attracted much attention in recent years because of its importance in homogeneous catalysis and in stereoselective, transition-metal-mediated, carbon–carbon bond formation.[1,2] A well-known example of carbon–hydrogen bond activation occurs in the orthometalation of C–H bonds of aryl-substituted phosphorus[1-3] and nitrogen ligands.[4] Activation of aliphatic carbon–hydrogen bonds of tolyl-[5,6] and alkylphosphine[6-8] ligands have also been reported. A schematic diagram of such activation is shown in eq 1.



(1)

Most C–H bond activation so far studied has been assisted by this "template effect" of the donor nitrogen or phosphorus atoms.

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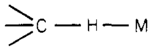
For orthometalation reactions, η_2-interaction of a phenyl ring may also assist activation.[9a] Interaction of the olefin with the metal center may be important in the cleavage of nonaromatic vinylic C–H bonds.[9b–d] It is possibly of importance for the activation of free naphthalene (HNp) to afford phosphine (P) complexes of the type $MH(Np)(P)_2$.[7a,8b,c,10] The iron members of this latter class of compounds are particularly active toward a variety of C_{sp}–H, C_{sp^2}–H, and, in active methylene complexes, C_{sp^3}–H bonds.[10] Activation of aromatic[11] and benzylic[12] C–H bonds by a bis(η^5-cyclopentadienyl)tungsten species has also been observed.

Although hydrogen–deuterium exchange for common alkanes or cycloalkanes has been studied,[13] there is little information concerning mechanistic and structural aspects of the activation of these relatively inert C_{sp^3}–H bonds. The primary step to such activation presumably involves the metal moiety approaching the C–H bond to within the sum of the van der Waals radii. Two limiting geometries, modes a and b, were proposed by Cotton et al.[14] The structures of a number of complexes with short M···H-C_{sp^3} separations have been determined.[14–19] In one example a three center–two electron-bonding scheme tending to mode a was inferred from the Mo···H–C angle of 136 (6)°.[14] In other examples a stronger tendency toward mode b has been observed.[16,17a]


a

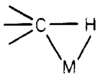

b

Table I. Crystal Data and Data Collection Details for 1

formula	$RuClC_{21}H_{25}$
formula weight	413.96
space group	C_i^1–$P\bar{1}$
a	7.389 (2) Å
b	13.271 (4) Å
c	9.439 (3) Å
α	105.37 (2)°
β	101.18 (2)°
γ	96.80 (2)°
V	861.3 Å^3
Z	2
ρ_{obsd}, ρ_{calcd}[a]	1.59 (1), 1.590 g cm^{-3}
temp	−150 °C[b]
cryst shape	parallelepiped, 0.63 × 0.50 × 0.11 mm
cryst vol	0.0363 mm^3
radiation	graphite-monochromated Mo Kα (λ(Mo Kα_1) = 0.7093 Å)
linear abs coeff	10.4 cm^{-1}
transmssn fact	0.594–0.895
detector aperture	5-mm wide, 6-mm high, 32 cm from crystal
takeoff angle	3.0°
scan speed	2.0° in 2θ/min
λ^{-1} sin θ limits	0.0431–0.7679 Å^{-1}, $3.5° < 2\theta < 66°$
bkgd counts	10 s at each end of scan, with rescan option[c]
scan range	1.3° below Kα_1 to 1.3° above Kα_2
data collctd	$\pm h, \pm k, l$
p	0.04
unique data	6762
unique data with $F_o^2 > 3\sigma(F_o^2)$	5788

[a] Flotation in aqueous $ZnCl_2$. The calculated density is for a crystal at room temperature with unit cell dimensions a = 7.42 Å, b = 13.21 Å, c = 9.38 Å, α = 103.3°, β = 101.2°, γ = 97.0° (film measurements). [b] The low-temperature system is based upon a design by Huffman, J. C. Ph.D. Thesis, Indiana University, 1976. [c] Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–571.

In this paper with the complexes [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)]chloro[3-(tricyclo[2.2.1.0^{2,6}]heptan-3-yl-κH^3)-*endo,endo*-bicyclo[2.2.1]hept-5-en-2-yl-(2,5,6-η)]ruthenium(II) and [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)][*endo*-3-(bicyclo[2.2.1]hept-5-en-2-yl-κH^2)-*endo,endo*-bicyclo[2.2.1]hept-5-en-2-yl-(2,5,6-η)]chlororuthenium(II) (norbonenyl–nortricyclyl and norbornenyl–norbornenyl compounds) we report the structural and spectroscopic characterization of the first examples of strong interaction between C_{sp^3}–H groups of relatively inert alicyclic hydrocarbon ligands and a metal center. These complexes are postulated to arise from an $RuHCl(NBD)_2$ intermediate via a double insertion mechanism which links together two norbornadiene moieties. We also report what we believe is the first *definitive* correlation of metal–olefin separations with C=C bond lengths.

Experimental Section

General Remarks. Proton NMR spectra were measured on JEOL C-60HL, PMX-60, FX-100, and CFT-20 spectrometers. Fourier transform carbon-13 spectra were obtained with a JEOL FX-100 spectrometer. Samples were dissolved in $CDCl_3$ solutions, and tetramethylsilane was used as an internal standard. Low-temperature (−105 °C) spectra were obtained with a CFT-20 spectrometer operating at 80 MHz with samples dissolved in toluene-d_8. Relaxation time measurements (10 wt % solutions in $CDCl_3$) were made with the use of a JEOL FX-60 spectrometer. Infrared spectra (KBr disks) were recorded on JASCO DS-403 or A-3 spectrometers.

The precursor complexes, $[RuCl_2(1,5\text{-cyclooctadiene})]_n$ and $[RuCl_2(NBD)]_n$, were prepared according to reported procedures.[18] Norbornadiene, purchased from Eastman Kodak Co., was purified by distillation. All manipulations were conducted in an atmosphere of dinitrogen.

Preparation of $RuClC_{21}H_{25}$ (1). To an acetonitrile (10 mL) suspension of $[RuCl_2(NBD)]_n$ (480 mg), zinc powder (3.98 g), and alumina (Merck 1097, 1 g) was added NBD (140 mg) with stirring. The mixture was refluxed for 30 min, and more NBD (140 mg) was added to the resultant

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orange suspension. Reflux was continued for an additional 18 min. The orange solution obtained was filtered and concentrated in vacuo. The oily product was chromatographed on alumina (Merck 1097; 15 mm i.d. × 150 mm) with ethyl ether as eluent. A pale yellow band was eluted first but this byproduct was extremely air-sensitive and decomposed immediately to a black oil. The orange band was eluted with methylene chloride and concentrated under reduced pressure. Addition of a small portion of ethyl ether produced orange crystals of RuClC$_{21}$H$_{25}$ (**1**). The product was completely crystallized by keeping the solution overnight in a refrigerator. Filtration of the product gave orange prisms of **1** in 48–50% yield.

A similar treatment of a suspension of [RuCl$_2$(1,5-cyclooctadiene)]$_n$ (560 mg), zinc powder (2 g), and NBD (620 mg) in refluxing acetonitrile gave **1** in 38% yield. As initially prepared, the product **1** contained two isomers in a 86:14 ratio. By repeated chromatography the percentage of the major isomer **1a** could be increased to 95%; mp 134–136 °C dec. Anal. Calcd for C$_{21}$H$_{25}$ClRu: C, 60.93; H, 6.09. Found: C, 61.04; H, 6.14. Ir (KBr): ν(C–H···Ru) 2580, ν(Ru–Cl) 239 cm^{-1}.

Preparation of [Ru(C$_{21}$H$_{25}$)(CH$_3$CN)][CF$_3$SO$_3$] (2). An acetonitrile (5 mL) solution of silver triflate (75 mg, 0.29 mmol) was added to an ethyl ether (10 mL) solution of **1** (122 mg, 0.29 mmol) at room temperature with stirring. A gray precipitate of silver chloride, which formed instantaneously, was filtered off. The yellow solution was concentrated in vacuo and chromatographed with an alumina column (10 mm i.d. × 20 mm) with the use of acetonitrile. The solution obtained was evaporated to an oil to which ethyl ether was added dropwise to give yellow prisms of complex **2** in 85% yield; mp 136–138 °C dec. Anal. Calcd for C$_{24}$H$_{28}$F$_3$NORuS: C, 50.70; H, 4.96; N, 2.46. Found: C, 50.74; H, 5.03; N, 2.57. Conductivity in an acetone solution (7.28 × 10^{-4} M), 1.18 × 10^2 M^{-1} Ω^{-1}, is indicative of a 1:1 electrolyte. Ir (KBr): ν(C–H···Ru) 2500, ν(CN) 2270, 2280 cm^{-1}; triflate group absorptions at 1270, 1145, and 1030 cm^{-1}. NMR (CDCl$_3$): δ −4.93 (1 H, br s), 0.9–1.2 (4 H, m, cyclopropane and metal–CH), 1.21 (2 H, m) and 1.3–1.8 (4 H, m) and 1.65 (2 H, m) for methylene bridges, 2.07 (1 H, br s, methine), 2.71 (1 H, m, methine), 3.08 (1 H, br) and 3.42 (1 H, m) for NBD bridgeheads, 2.65 (2 H, m, bridgeheads of ring B), 3.90 (2 H, m), 4.10 (1 H, m), 4.28 (2 H, m), and 6.05 (1 H, m) for coordinated olefins, 2.45 (3 H, s, CH$_3$CN).

Crystallographic Study of RuClC$_{21}$H$_{25}$ (1). Triclinic symmetry was established by precession and Weissenberg photography. Space group $P\bar{1}$ was assumed, and the subsequent successful elucidation and refinement of the structure vindicated this assumption. The crystal selected for data collection at −150 °C upon a Picker FACS-I automatic diffractometer was cleaved from a much larger crystal. Crystal mosaicities (peak widths at half-peak height), as determined by ω scans, were typically in the range 0.16–0.22° for intense, low-angle reflections. Lattice parameters were obtained as previously described[19] by the hand centering of 19 reflections in the range $0.4818 < \lambda^{-1} \sin \theta < 0.5048$ Å^{-1} with Mo Kα_1 radiation (λ = 0.7093 Å). Important details of data collection are summarized in Table I. Because difficulties were encountered, more detail than usual is provided to describe the solution and refinement of this structure.

Standard procedures and programs were used to solve and refine the structure.[19] In the initial stages calculations were done with use of the CDC 6600 computer at Northwestern University. The Lawrence Berkeley Laboratory's CDC 7600 computer was used for final refinements. Coordinates for the ruthenium and chlorine atoms were deduced from an unsharpened Patterson map. The positions of carbon atoms were then obtained from a Fourier synthesis with phases derived from the contribution of ruthenium and chlorine atoms. After further refinement, all hydrogen atoms were unambiguously located and included in the model at their observed positions as a fixed contribution.

Constraints on the thermal motion of nonhydrogen atoms were relaxed, but least-squares refinement failed to disperse electron density in the vicinity of a nortricyclyl residue. Closer investigation of electron density maps showed that two chemically distinct species are present in the crystal. The major component, **1a**, the nortricyclyl derivative, is illustrated in Figure 1a along with the atom labeling scheme for the whole molecule. Figure 1b illustrates the minor component, the norbornenyl derivative, **1b**. Atoms C(17), C(18), and C(19) together with their hydrogen atoms were assigned a variable occupancy α; atoms C(22), C(23), and C(24) were constrained to occupancy 1-α, and allowed only an isotropic model for their thermal motion. Other atoms in the minor component appeared to be almost, if not exactly, coincident with atoms C(15), C(16), C(19), and C(21) of the major component; these atoms were given an occupancy of 1.0. Upon refinement, the values for R and R_w were lowered from 0.037 and 0.049 (prior to addition of the minor component) to 0.033 and 0.043. Hydrogen atoms were now allowed to refine isotropically. The final model for the structure, which was described by 322 variable parameters, was refined with the use of all data, including $F_o^2 < 0$, to a very satisfactory convergence. The final values for R and R_w on F^2 are 0.050 and 0.072; for data having $F_o^2 \geq 3\sigma(F_o^2)$ the values for R and R_w on F are 0.028 and 0.036. The standard error in an observation of unit weight is 1.32 e^2. The final value for α is 0.862 (5). Table II contains the final atomic parameters. Table III[20] lists values of $10|F_o|$ and $10|F_c|$. A negative value for F_o denotes $F_o^2 < 0$.

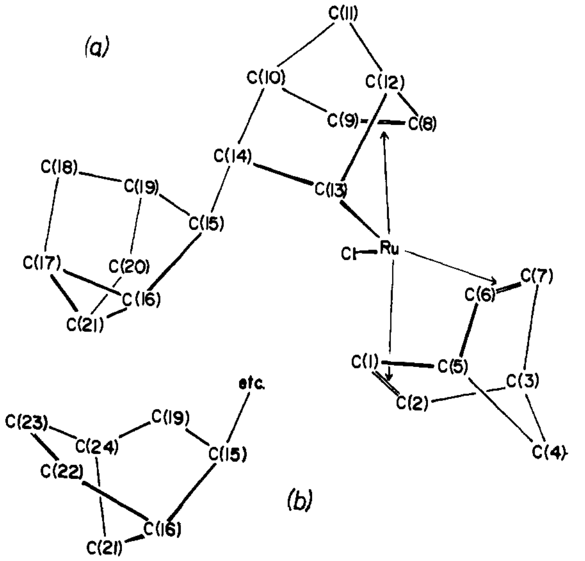

Figure 1. The atom labeling scheme for **1**. The orientation indicated here is rotated approximately 90° from that for Figure 2. The minor component (b) is shown with approximately the same orientation as that for the major component (a).

Results

General Description of the Structure. The crystal studied was actually an admixture of two chemically distinct compounds differing only in the nature of the third noncoordinated norbornadiene residue. Figure 1 illustrates the two components. The molecular structure of the major component, **1a**, is shown in Figure 2. With reference to Figure 1a, it may be seen that the complex comprises a chloro ligand, a doubly coordinated norbornadiene ligand, and a nortricyclyl–norbornenyl group formed from two norbornadiene molecules. The olefin of the norbornenyl moiety is coordinated weakly to the ruthenium atom. The termini of the other double bond of its norbornadiene parent are involved in a ruthenium–alkyl σ bond approximately trans to the chloro group and in an endo linkage with another norbornadiene molecule, which also suffers a protonation and cyclopropanation to become the nortricyclyl fragment.

The minor component, **1b**, present at 14%, is shown in Figure 1b. The nortricyclyl group of **1a** is replaced by a norbornenyl group. The presence of this minor component has no discernible effect on the geometry around the metal center. Indeed, if the diffraction data had not been collected at low temperature the minor component might well have escaped detection and been dismissed in the crystal structure as unusually high thermal motion and/or irresolvable disorder of the nortricyclyl moiety and in spectroscopic studies as an unidentifiable impurity. This minor component is of considerable importance in analyzing possible reaction mechanisms for the formation of both **1b** and **1a**.

The crystal packing, illustrated in Figure 3 for the major component, is unremarkable with no contacts among nonhydrogen atoms less than 3.514 (3) Å. The minor component packs comfortably into the host lattice with no contacts between it and the major component shorter than 3.38 (2) Å. However, from Tables IV[20] and V[20] of nonbonded contacts it is apparent that the minor component is unlikely to coexist alongside itself in the present crystal structure. Bond distances and angles for nonhydrogen atoms are tabulated in Tables VI and VII. The large data set encouraged us to refine hydrogen atom positions, and hence we are dealing with hydrogen atom positions which are as unbiased

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[20] Supplementary material.

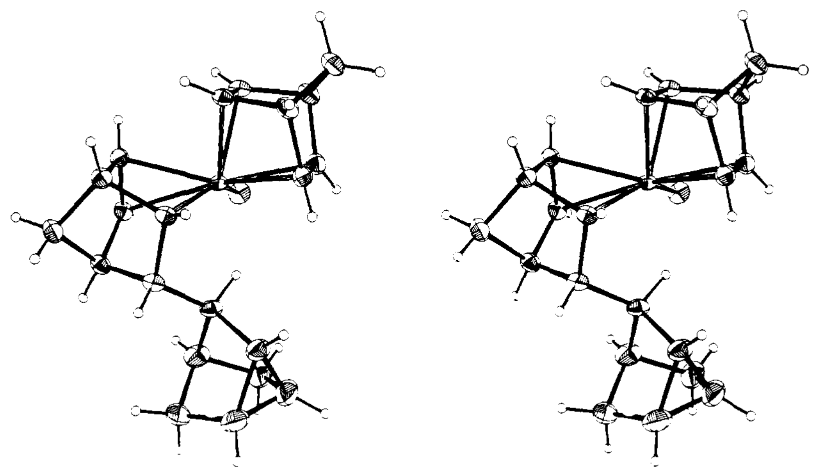


Figure 2. Stereodiagram of **1a**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn artificially small.

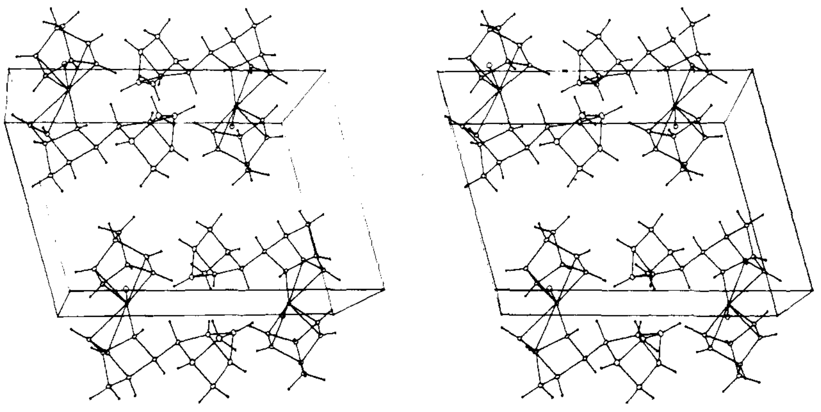
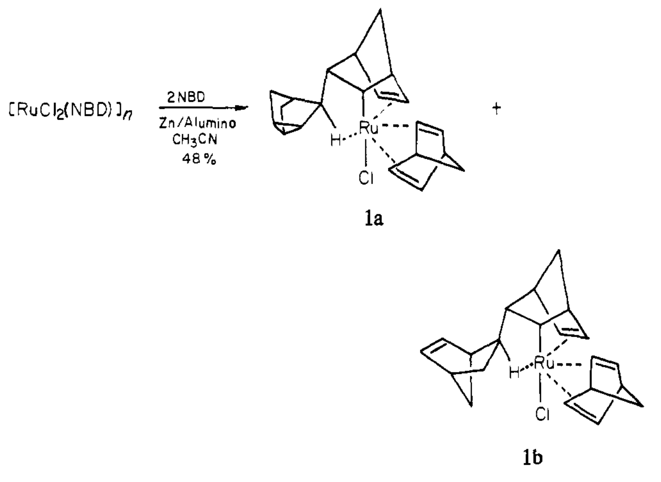


Figure 3. Stereodiagram of the packing of **1a** in the unit cell. Hydrogen atoms are drawn artificially small.

as possible. Bond distances and angles involving hydrogen atoms are given in Tables VIII[20] and IX;[20] the scatter for C–H separations about their mean value is not significant in relation to the estimated standard deviation of an individual C–H separation as obtained from the inverse of the least-squares matrix.

In a later section the molecular stereochemistry, particularly the unusually close Ru···H contact, will be discussed in more detail in conjunction with the chemical and other physical properties of this compound.

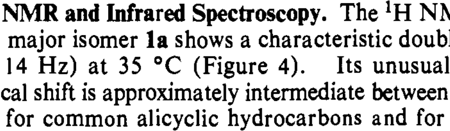
Preparation. Refluxing an acetonitrile suspension of $[RuCl_2(NBD)]_n$[18] with norbornadiene (NBD) in the presence of zinc powder and alumina produced compounds **1a** and **1b**, as determined by X-ray analysis. The results of this analysis show that there is a stereospecific endo linking of NBD units with respect to the norbornenyl ring common to **1a** and **1b**. In **1b** an endo–endo arrangement of the two norbornene units is observed. In **1a**, as discussed later, the nortricyclyl–norbornenyl moiety also arises from a stereospecific endo–endo association of the parent NBD molecules.



1a

1b

When the major isomer (**1a**) was treated with an acetonitrile solution of silver triflate, a cationic complex, $[Ru(C_{21}H_{25})(CH_3CN)][CF_3SO_3]$ (**2**), was isolated in 85% yield. The similar pattern for the ^1H and ^{13}C NMR spectra for **1a** and **2** indicate a closely related stereochemistry. For **2** the ^1H resonances, with the exception of the high field C–H···Ru signal and the lowest field olefinic resonance, are shifted downfield with respect to **1a**, as expected for a cationic complex.



2

^{1}H NMR and Infrared Spectroscopy. The ^1H NMR spectrum of the major isomer **1a** shows a characteristic doublet at δ −3.74 (J = 14 Hz) at 35 °C (Figure 4). Its unusually high-field chemical shift is approximately intermediate between the chemical shifts for common alicyclic hydrocarbons and for terminal ruthenium(II) hydrides.[21] An alicyclic C–H bond therefore appears to be interacting with the ruthenium center. Variable-temperature measurements from 35 to −105 °C revealed essentially no change in the spectral pattern, except for this high-field doublet which shifted further upfield (δ −3.74 at 35 °C, −3.94 at −29 °C, and

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[21] (a) Jesson, J. P. *Transition Met. Hydrides* **1971**, *1*, 117. (b) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 189–290.

Table II. Positional and Thermal Parameters for the Atoms of 1

ATOM	X[A]	Y	Z	B11 OR B, $Å^2$[B]	B22	B33	B12	B13	B23
RU	0.21804(1)	0.188912(9)	-0.03240(1)	36.2(2)	18.60(8)	37.0(2)	5.23(8)	4.3(1)	10.14(7)
CL	-0.11159(5)	0.16729(3)	-0.00726(5)	48.6(6)	34.7(2)	80.1(5)	7.6(3)	24.2(4)	16.9(3)
C(1)	0.4138(2)	0.3215(1)	0.1412(2)	77.(3)	23.1(8)	47.(2)	4.(1)	0.(2)	7.2(10)
C(2)	0.2531(2)	0.2977(1)	0.1927(2)	79.(3)	29.9(9)	47.(2)	15.(1)	9.(2)	7.(1)
C(3)	0.2925(2)	0.2150(2)	0.2770(2)	81.(3)	41.(1)	41.(2)	11.(1)	16.(2)	16.(1)
C(4)	0.5044(3)	0.2521(2)	0.3483(2)	98.(3)	42.(1)	41.(2)	13.(1)	3.(2)	12.(1)
C(5)	0.5535(2)	0.2559(1)	0.1980(2)	60.(2)	30.4(9)	45.(2)	3.(1)	-1.(2)	11.2(10)
C(6)	0.4552(2)	0.1463(1)	0.0931(2)	54.(2)	27.1(9)	44.(2)	12.(1)	4.(2)	14.9(9)
C(7)	0.2911(2)	0.1195(1)	0.1427(2)	69.(3)	28.8(9)	51.(2)	10.(1)	10.(2)	21.(1)
C(8)	0.2277(2)	0.0348(1)	-0.1993(2)	75.(3)	21.1(8)	44.(2)	7.(1)	5.(2)	7.5(9)
C(9)	0.0815(2)	0.0712(1)	-0.2750(2)	58.(2)	24.8(8)	44.(2)	2.(1)	0.(2)	7.0(9)
C(10)	0.1557(2)	0.1226(1)	-0.3854(2)	69.(3)	30.7(9)	40.(2)	9.(1)	4.(2)	11.7(10)
C(11)	0.3168(2)	0.0626(2)	-0.4146(2)	90.(3)	37.(1)	43.(2)	15.(1)	17.(2)	9.(1)
C(12)	0.4005(2)	0.0799(1)	-0.2458(2)	61.(2)	28.8(9)	47.(2)	13.(1)	12.(2)	11.6(10)
C(13)	0.4052(2)	0.2001(1)	-0.1712(2)	47.(2)	26.1(8)	43.(2)	5.(1)	5.(1)	13.3(9)
C(14)	0.2685(2)	0.2332(1)	-0.2902(2)	65.(2)	28.7(9)	46.(2)	8.(1)	10.(2)	18.5(10)
C(15)	0.1477(2)	0.3118(1)	-0.2229(2)	74.(3)	25.3(9)	57.(2)	10.(1)	-1.(2)	19.(1)
C(16)	0.2414(3)	0.4279(1)	-0.1789(2)	131.(4)	23.2(9)	70.(2)	2.(1)	-14.(2)	12.(1)
C(17)	0.1784(4)	0.4665(2)	-0.3171(3)	207.(6)	31.(1)	88.(3)	13.(2)	-5.(3)	24.(2)
C(18)	0.0485(4)	0.3735(2)	-0.4370(3)	165.(5)	44.(2)	57.(2)	34.(2)	-2.(3)	21.(2)
C(19)	-0.0326(3)	0.3197(2)	-0.3324(2)	90.(3)	39.(1)	84.(2)	18.(2)	-16.(2)	20.(1)
C(20)	-0.0958(4)	0.4173(2)	-0.2311(3)	154.(5)	50.(2)	89.(3)	55.(2)	9.(3)	13.(2)
C(21)	0.0868(4)	0.4920(2)	-0.1872(3)	213.(5)	34.(1)	80.(2)	39.(2)	-11.(3)	8.(1)
C(22)	0.310(2)	0.440(1)	-0.331(2)	2.3(2)					
C(23)	0.140(2)	0.439(1)	-0.426(2)	2.0(2)					
C(24)	-0.009(2)	0.421(1)	-0.358(2)	2.6(3)					
H(C1)	0.438(3)	0.380(2)	0.105(2)	1.2(4)					
H(C2)	0.156(4)	0.340(2)	0.203(3)	2.1(5)					
H(C3)	0.209(3)	0.201(2)	0.339(2)	1.2(4)					
H1(C4)	0.528(4)	0.322(2)	0.427(3)	2.4(5)					
H2(C4)	0.561(4)	0.196(2)	0.385(3)	2.2(5)					
H(C5)	0.680(3)	0.279(2)	0.198(2)	1.5(4)					
H(C6)	0.519(3)	0.098(2)	0.039(3)	1.7(4)					
H(C7)	0.218(3)	0.051(2)	0.118(2)	1.4(4)					
H(C8)	0.220(3)	-0.015(2)	-0.151(3)	1.7(4)					
H(C9)	-0.053(3)	0.053(2)	-0.278(3)	1.8(4)					
H(C10)	0.053(4)	0.120(2)	-0.478(3)	2.2(5)					
H1(C11)	0.399(4)	0.093(2)	-0.469(3)	2.3(5)					
H2(C11)	0.275(4)	-0.010(2)	-0.474(3)	2.9(6)					
H(C12)	0.507(4)	0.054(2)	-0.212(3)	1.8(5)					
H(C13)	0.527(4)	0.246(2)	-0.127(3)	2.3(5)					
H(C14)	0.325(4)	0.258(2)	-0.351(3)	2.1(5)					
H(C15)	0.103(4)	0.299(2)	-0.130(3)	2.3(5)					
H(C16)	0.359(4)	0.457(2)	-0.105(3)	3.8(7)					
H(C17)	0.259(6)	0.519(3)	-0.352(4)	4.1(9)					
H1(C18)	-0.047(6)	0.402(3)	-0.494(4)	3.2(8)					
H2(C18)	0.107(6)	0.324(3)	-0.506(4)	3.3(8)					
H(C19)	-0.115(4)	0.261(2)	-0.365(3)	3.0(6)					
H1(C20)	-0.128(6)	0.407(3)	-0.156(5)	4.2(10)					
H2(C20)	-0.191(6)	0.445(3)	-0.294(5)	4.1(9)					
H(C21)	0.108(5)	0.565(3)	-0.138(4)	4.0(7)					

[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.

−4.06 at −105 °C), indicating a greater interaction between the alicyclic C–H bond and the metal center at low temperatures. Furthermore, in the infrared spectrum of **1a** an extremely low ν_{C-H} frequency is observed at 2580 cm^{-1}. Common alicyclic and olefinic absorptions occur in the range 2840–3050 cm^{-1}.

The high-field signal of the minor isomer **1b** appears as a broad multiplet centered at δ −2.84, indicating a weaker Ru···H interaction than that found for the major isomer **1a**. On the other hand, Table **VI**. Bond Distances (Å) among Nonhydrogen Atoms of 1

atoms	dist	atoms	dist
Ru–Cl	2.4831 (8)	C(12)–C(13)	1.557 (2)
Ru–C(13)	2.099 (2)	C(13)–C(14)	1.550 (2)
Ru–C(1)	2.196 (2)	C(14)–C(10)	1.542 (2)
Ru–C(2)	2.176 (2)	C(14)–C(15)	1.542 (2)
Ru–C(6)	2.140 (2)	C(15)–C(16)	1.524 (3)
Ru–C(7)	2.110 (2)	C(11)–C(12)	1.535 (3)
Ru–C(8)	2.245 (2)	C(16)–C(21)	1.505 (3)
Ru–C(9)	2.353 (2)	C(17)–C(21)	1.494 (4)
Ru···H(15)	2.10 (3)	C(17)–C(18)	1.511 (4)
C(1)–C(2)	1.400 (2)	C(18)–C(19)	1.532 (3)
C(6)–C(7)	1.422 (2)	C(19)–C(15)	1.553 (3)
C(8)–C(9)	1.385 (2)	C(19)–C(20)	1.571 (3)
C(1)–C(5)	1.535 (2)	C(20)–C(21)	1.491 (4)
C(2)–C(3)	1.540 (3)		
C(5)–C(6)	1.527 (2)	Minor Component	
C(3)–C(7)	1.534 (3)	C(16)–C(22)	1.655 (15)
C(3)–C(4)	1.543 (3)	C(22)–C(23)	1.389 (20)
C(4)–C(5)	1.543 (2)	C(23)–C(24)	1.405 (21)
C(8)–C(12)	1.535 (2)	C(24)–C(21)	1.470 (10)
C(9)–C(10)	1.537 (2)	C(24)–C(19)	1.428 (16)
C(10)–C(11)	1.537 (2)		
C(1)–C(12)	1.538 (2)		

in the cationic complex **2**, the chemical shift of this proton signal is further upfield at δ −4.93 at 25 °C. The ν_{C-H} frequency also shifts to 2500 cm^{-1}. These spectral data clearly indicate a greater interaction between the alicyclic C–H bond and the ruthenium(II) moiety upon conversion to the cationic complex.

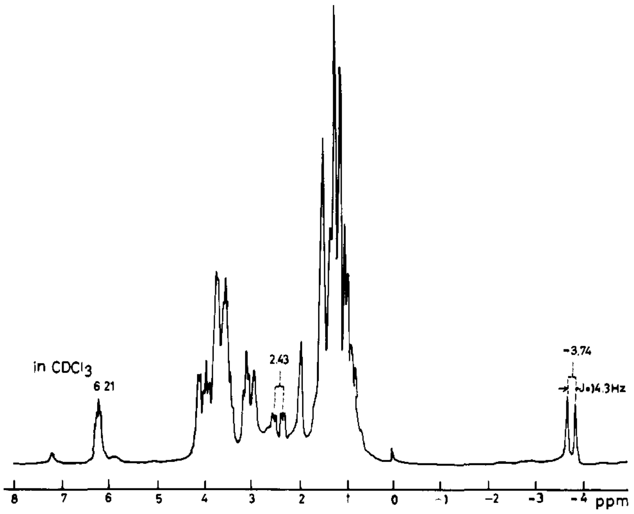


Figure 4. ^{1}H NMR spectrum of **1a** in CDCl$_3$ at 35 °C.

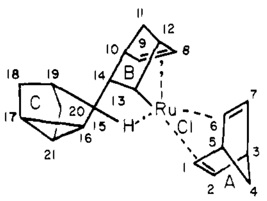
The assignments of the complex ^{1}H NMR spectrum (Table X) of the major isomer **1a** are based on the X-ray structure and the following decoupling results. When the high-field doublet of **1a** at δ −3.74 was irradiated, the doublet of double doublets, *J*(1) = 14, *J*(2) = 4, and *J*(3) < 2 Hz, at δ 2.43 turned to a double doublet with loss of the 14-Hz coupling. Irradiation of the latter signal (i) sharpened the multiplets at δ 3.41 and 3.76 by removing the 4 Hz coupling, (ii) decoupled the high-field doublet, and (iii) decoupled the doublet at δ 0.90 with *J* < 2 Hz. On this basis the multiplets at δ 3.41 and 3.76 are assigned to H(12) and H(10) of the norbornene ring B and the signal at δ 0.9 to H(13) whose

Table **VII**. Bond Angles (Deg) among Nonhydrogen Atoms of 1

atoms	angle	atoms	angle	atoms	angle
		(a) Coordination Sphere			
Cl–Ru–C(13)	148.04 (4)	C(10)–Ru–C(9)	157.50 (6)	Ru–C(18)–C(12)	94.50 (9)
Cl–Ru–C(1)	115.65 (5)	C(2)–Ru–C(6)	78.14 (7)	Ru–C(9)–C(10)	68.25 (8)
Cl–Ru–C(2)	79.93 (5)	C(2)–Ru–C(7)	66.40 (7)	Ru–C(9)–C(8)	105.59 (9)
Cl–Ru–C(6)	128.72 (5)	C(2)–Ru–C(8)	154.95 (6)	Ru···H(C15)–C(15)	118 (2)
Cl–Ru–C(7)	89.63 (5)	C(2)–Ru–C(9)	162.16 (6)	B–Ru–A	69.8 (1)^a
Cl–Ru–C(8)	103.35 (5)	C(6)–Ru–C(8)	80.79 (6)	B–Ru–C	101.6 (1)
Cl–Ru–C(9)	82.46 (5)	C(6)–Ru–C(9)	115.71 (6)	B–Ru–C(13)	99.40 (9)
C(1)–Ru–C(2)	37.34 (6)	C(7)–Ru–C(8)	85.67 (7)	B–Ru–Cl	109.32 (7)
C(6)–Ru–C(7)	39.09 (6)	C(7)–Ru–C(9)	116.47 (7)	B–Ru···H(C15)	159.6 (6)
C(8)–Ru–C(9)	34.96 (6)	Ru–C(13)–C(14)	95.78 (9)	H(C15)···Ru–A	89.7 (6)
C(17)–Ru–C(11)	86.58 (7)	Ru–C(13)–C(12)	99.71 (9)	H(C15)···Ru–C	98.2 (6)
C(13)–Ru–C(2)	123.72 (7)	Ru–C(1)–C(2)	70.57 (9)	H(C15)···Ru–C(13)	87.1 (8)
C(13)–Ru–C(6)	80.61 (6)	Ru–C(1)–C(5)	97.23 (9)	H(C15)···Ru–Cl	76.0 (8)
C(13)–Ru–C(7)	118.39 (6)	Ru–C(2)–C(13)	95.49 (9)	A–Ru–C	168.05 (9)
C(13)–Ru–C(8)	65.10 (6)	Ru–C(2)–C(1)	72.09 (9)	A–Ru–C(13)	105.07 (8)
C(13)–Ru–C(9)	71.70 (6)	Ru–C(6)–C(7)	69.30 (9)	A–Ru–Cl	79.91 (7)
C(1)–Ru–C(6)	64.57 (7)	Ru–C(6)–C(5)	99.8 (1)	C–Ru–C(13)	67.42 (8)
C(1)–Ru–C(7)	66.40 (7)	Ru–C(7)–C(6)	98.4 (1)	C–Ru–Cl	92.76 (6)
C(1)–Ru–C(8)	138.61 (6)	Ru–C(7)–C(3)	71.6 (1)	C(13)–Ru–Cl	148.04 (4)
		Ru–C(8)–C(9)	76.79 (9)		
		(b) Ligand			
C(5)–C(1)–C(2)	106.0 (1)	C(9)–C(10)–C(14)	106.6 (1)	C(20)–C(21)–C(17)	107.5 (2)
C(1)–C(2)–C(3)	106.4 (1)	C(8)–C(12)–C(13)	98.4 (1)	C(16)–C(21)–C(17)	61.6 (2)
C(5)–C(6)–C(7)	106.5 (1)	C(10)–C(11)–C(12)	93.8 (1)	C(17)–C(18)–C(19)	98.2 (2)
C(6)–C(7)–C(3)	105.2 (1)	C(12)–C(13)–C(14)	104.4 (1)	C(15)–C(19)–C(18)	101.9 (2)
C(2)–C(3)–C(4)	100.9 (1)	C(13)–C(14)–C(10)	99.3 (1)	C(15)–C(19)–C(20)	100.9 (2)
C(7)–C(3)–C(4)	101.7 (1)	C(13)–C(14)–C(15)	114.3 (1)	C(18)–C(19)–C(20)	99.4 (2)
C(4)–C(5)–C(6)	101.5 (1)	C(10)–C(14)–C(15)	114.0 (1)	C(19)–C(20)–C(21)	97.2 (2)
C(4)–C(5)–C(1)	101.8 (1)	C(14)–C(15)–C(16)	113.6 (2)		
C(2)–C(3)–C(7)	99.6 (1)	C(14)–C(15)–C(19)	116.6 (1)	Minor Component	
C(1)–C(5)–C(6)	98.4 (1)	C(16)–C(15)–C(19)	97.3 (2)	C(15)–C(16)–C(22)	104.4 (5)
C(3)–C(4)–C(5)	94.0 (1)	C(15)–C(16)–C(19)	106.3 (2)	C(21)–C(16)–C(22)	97.8 (5)
C(12)–C(8)–C(9)	104.1 (1)	C(15)–C(16)–C(21)	106.9 (2)	C(16)–C(21)–C(24)	91.5 (6)
C(8)–C(9)–C(10)	108.0 (1)	C(17)–C(16)–C(21)	58.9 (2)	C(16)–C(22)–C(23)	101 (1)
C(9)–C(10)–C(11)	101.0 (1)	C(16)–C(17)–C(18)	106.6 (2)	C(22)–C(23)–C(24)	111 (1)
C(14)–C(10)–C(11)	100.2 (1)	C(18)–C(17)–C(21)	106.3 (2)	C(23)–C(24)–C(21)	99 (1)
C(11)–C(12)–C(8)	100.2 (1)	C(16)–C(17)–C(21)	59.6 (2)	C(19)–C(24)–C(21)	98.3 (9)
C(11)–C(12)–C(13)	104.0 (1)	C(20)–C(21)–C(16)	108.0 (2)	C(23)–C(24)–C(19)	113 (1)

[a] For this and subsequent entries, A is defined as the midpoint of the bond C(1)–C(2), B the midpoint of C(6)–C(7), and C the midpoint of C(8)–C(9).

Table X. ^{1}H NMR Data of the Major Isomer (1a)



ring	assignment		chem shift,[a] δ
A	olefinic	H(1)	3.96 (1 H, t, $J = 4$ Hz)
		H(2)	3.72 (1 H, m)
		H(6), H(7)	3.56 (2 H, m)
	bridgehead	H(3)	2.94 (1 H, br s)
		H(5)	3.12 (1 H, t, $J = 4$ Hz)
	bridge	H(4)	1.52 (2 H, br s)
B	olefinic	H(8)	4.11 (1 H, m)
		H(9)	6.21 (1 H, dt, $J = 4$ Hz, $J' = 1$ Hz)
	bridgehead	H(10)	3.76 (1 H, m)
		H(12)	3.41 (1 H, m)
	bridge	H(11)	1.29 (2 H, br s)
	methine	H(14)	2.43 (1 H, ddd, $J(15) = 14$, $J(10) = 4$, $J(13) = 1$–2 Hz)
		H(13)	0.90 (1 H, d, $J(14) = 1$–2 Hz)
C	methylene	H(18), H(20)	1.5–1.2 (4 H, m)
	methine	H(19)	1.98 (1 H, br s)
		H(15)	−3.74 (1 H, d, $J = 14$ Hz)
	cyclopropane	H(16), H(17), H(21)	1.1–0.6 (3 H, m)

[a] Solvent $CDCl_3$.

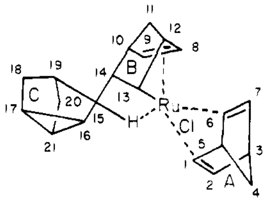
carbon atom is σ bonded to the ruthenium center. The lowest field multiplet at δ 6.21 is assigned to the most weakly coordinated olefin proton H(9) in ring B. Irradiation at δ 6.21 sharpened the multiplet at δ 3.76, assigned to H(10).

In the ^{1}H NMR spectrum of the admixture of **1a** and **1b**, additional olefinic protons H(21) and H(22) of the minor isomer **1b** appear as multiplets at δ 5.83, a value close to that of δ 5.94 of free norbornene.[22]

^{13}C NMR Spectroscopy. The ^{13}C NMR spectrum of **1a** shows 21 signals under complete proton decoupling in $CDCl_3$. Chemical shifts and relaxation times are summarized in Table XI. Signals at 26.1, 34.0, 54.6, and 56.3 ppm are assigned to the four methylene carbon atoms based on (i) the partial proton decoupling experiments, which clearly indicate that these signals split into triplets, and (ii) the extremely short relaxation times, 0.36–0.45 s, of the signals. The bridging carbon signals of norbornadiene and 5-*endo*-methylnorbornene have been reported at 75.4 and 50.5 ppm, respectively.[23] When NBD is coordinated, these signals have been observed to shift to lower field (62.5–65.5 ppm).[24,25] The signals at 56.3 and 54.6 ppm, therefore, are assigned to the bridging carbon atoms C(4) and C(11), respectively. The remaining two methylene signals at 34.0 and 26.1 ppm are assigned to the two nortricyclane methylene carbon atoms, C(18) and C(20), since in unsubstituted nortricyclane these signals appear at 33.1 ppm.[23] High-field signals at 10.7, 12.5, and 15.4 ppm are ascribed to the cyclopropane carbon atoms C(16), C(17), and C(21) by analogy to the reported value of 9.9 ppm for nortricyclane.[23]

Other signals were assigned by means of the selective $\{^1H\}^{13}C$ experiments. For example, irradiation of the high-field proton doublet at δ −3.74 resulted in enhancement of the C(15) signal at 35.8 ppm—this signal had shown the longest relaxation time indicative of substantial perturbation of the C(15)–H bond by the ruthenium moiety. Bridgehead carbon atoms, C(3) and C(5) for the coordinated NBD (ring A) and C(10) and C(12) for the norbornene skeleton (ring B), were associated with signals at 45.2 and 44.0, and 50.0 and 48.8 ppm, respectively, because these signals were enhanced upon irradiation of the corresponding proton resonances at δ 2.94 and 3.12, and 3.76 and 3.41. The olefinic proton signals of the weakly coordinated double bond C(8)=C(9) at δ 6.21 and 4.11 were found to correspond to the carbon signals at 121.2 and 90.9 ppm, on the basis of their selective irradiation. Four carbon resonances in the range 46.8–65.9 ppm, which are intermediate between 76.6–79.6 ppm for $M(NBD)(CO)_3$, M = Cr and Mo,[25] and 28.9 ppm for $Rh(NBD)(\eta^5\text{-}C_5H_5)$,[26] are assigned to the NBD olefin carbon atoms.

Table XI. ^{13}C Data of the Major Isomer (1a)



ring	assignments		chem shift, ppm[a]	relax time, s
A	olefinic	C(1)	65.9	0.89
		C(2)	60.9	0.80
		C(6)	53.4	0.77
		C(7)	46.8	0.70
	bridgehead	C(3) and C(5)	45.2	0.83
			44.0	0.82
	bridge	C(4)	56.3	0.45
B	olefinic	C(8)	90.7	0.73
		C(9)	121.2	0.67
	bridgehead	C(10)	50.0	0.81
		C(12)	48.8	0.87
	bridge	C(11)	54.6	0.45
	Ru–C σ bond	C(13)	19.5	0.85
	methine	C(14)	52.2	0.93
C	cyclopropane	C(16), C(17), and C(21)	15.4	0.75
			12.5	0.89
			10.7	0.82
	methylene	C(18) and C(20)	34.0	0.44
			26.1	0.36
	methine	C(15)	35.8	1.03
		C(19)	34.7	0.81

[a] Solvent $CDCl_3$. Downfield from internal tetramethylsilane.

The ^{13}C NMR spectrum of the minor isomer, **1b**, was obtained by subtracting the resonances of the major isomer, **1a**, from the spectrum of a crude mixture composed of 71% of **1a** and 29% of **1b**. The results are summarized in Table XII. The characteristic feature of the ^{13}C NMR spectrum of **1b** is the presence of the free olefinic carbon resonances at 140.8 and 130.4 ppm instead of the cyclopropane carbon resonances for ring C in **1a**.

Discussion

The Ru···HCR_3 Interaction. Although the cyclopropyl group is known to stabilize cyclopropylcarbinyl cations, the cyclopropyl group in nortricyclane activates an α-C–H bond less than do heteroatoms or conjugated systems; and the norbornenyl moiety in **1b** is even less activating. The structural and spectral results reported here on the ruthenium complex **1** appear, therefore, to document the first example of substantial interaction of a metal atom with a relatively inert C–H moiety. The ruthenium-hydrogen separation in the mixture of 86% of **1a** and 14% of **1b** is 2.10 (3) Å, and the angle Ru···H–C(15) is 118 (2)°. This particular hydrogen atom occupies a coordination site which is

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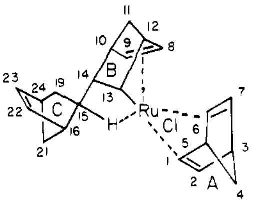
Table XII. ^{13}C NMR Data of the Minor Isomer (1b)



ring	assignment		chem. shift, ppm^a
A	olefinic	C(1)	67.4
		C(2)	62.5
		C(6)	49.8
		C(7)	48.2
	bridgehead	C(3), C(5)	43.3, 42.3
	bridge	C(4)	56.5
B	olefinic	C(8)	92.1
		C(9)	122.6
	bridgehead	C(10), C(12)	49.8, 48.2
	bridge	C(11)	54.9
	Ru-C σ bond	C(13)	20.4
	methine	C(14)	52.5
C	olefinic	C(22), C(23)	140.8, 130.4
	bridgehead	C(16), C(24)	47.9, 46.2
	methylene	C(19), C(21)	32.9, 32.1
	methine	C(15)	35.8

^{a} See text; measured in CDCl$_3$.

pseudotrans to the tightly coordinated double bond C(5)=C(6), of the coordinated NBD ligand. For **1b** in solution there is a peak at δ −2.83 in the ^{1}H NMR spectrum, evidence for substantial Ru···H interaction. Thus, the conformation of the dangling norbornenyl residue for **1b**, which leads to a Ru···H separation indistinguishable from that observed for **1a**, is not entirely a consequence of the major isomer **1a** dictating the conformation of the minor isomer **1b** in the solid state. Interaction of this hydrogen atom H(15) with the ruthenium center is therefore not peculiar to the cyclopropylcarbinyl system of the nortricyclane skeleton in the major isomer **1a**.

There have been only a few structure determinations which demonstrate the interaction of a transition metal with a carbon-hydrogen bond. Cotton et al. appear to be the first to report a short metal-hydrogen distance, Mo···H = 2.27 (8) Å, involving an α-C-H group of the borate species for the complex [BEt$_2$(Pz)$_2$][Mo(CO)$_2$(η^3-CH$_2$CPhCH$_2$)].[14] A Ru···H(phenyl) separation of 2.2 Å has been calculated for a five-coordinate ruthenium complex.[27] In recent work by Williams et al.,[16] an extremely short distance of 1.874 (3) Å between a cyclic alkenyl ligand and the iron center in the complex [Fe(P(OCH$_3$)$_3$)$_3$(η^3-C$_8$H$_{13}$)]$^+$ was observed, along with a long C-H separation of 1.164 (3) Å. In all these cases the C-H bonds interacting with the metal have α-functionalities such as a boron atom or an enyl group.

The C(15)-H bond is the longest in complex **1**, but is not significantly so. Because of the usual foreshortening of C-H bonds in measurements arising from X-ray data, the C(15)-H separation of 1.04 (3) Å almost certainly represents a lower bound and the Ru···H separation of 2.10 (3) Å an upper bound. Further definitive evidence for substantial perturbation of the C(15)-H bond upon interaction with the ruthenium center is also provided by the following observations: (i) an extremely long relaxation time for the C(15) signal in the ^{13}C NMR spectrum of **1a**, (ii) the appearance of a band at 2580 cm^{-1}, which we assign to $\nu_{\text{C-H}}$, and (iii) the relatively large coupling constant, $J_{\text{H(15)-H(14)}}$ = 14 Hz in the ^{1}H NMR spectrum. Furthermore, in the cationic complex **2**, there is evidence (see above) of even greater interaction between an alicyclic C-H bond and the ruthenium(II) atom. These C(15)-H···**Ru** moieties are examples of incipient, if not actual, two-electron-three-center bonds which have been postulated as a primary step towards the activation of hydrocarbon C-H bonds.

The Ruthenium-Olefin Moiety. Table XIII summarizes some metrical details for selected ruthenium-olefin,[28-32] -chloro,[28,29,32] and -alkyl[7b,30,31,33] complexes and for various combinations thereof.

Correlation of metal-olefin bond lengths with olefin C=C bond lengths, as an indicator of the extent of metal-olefin bonding, has long been suspected[34] but has rarely been convincingly established either because of relatively high errors associated with the C=C bond distance or because of dangers inherent in comparing one structure with another. Because tris(olefin) complexes are rare,[34] we have here an unusual opportunity to correlate the M-C distances with the C=C distances, especially in view of the high precision of the structure determination and the marked asymmetry of complex **1**. The Ru-C$_{\text{olefin}}$ distances (Ru-C(6) and Ru-C(7)) trans to the semivacant coordination site observed for **1** are the shortest known. Reassuringly, the C=C bond length (C(6)-C(7)) of this olefin is significantly longer than the other two. The Ru-C$_{\text{olefin}}$ distances of intermediate magnitude (Ru-C(1) and Ru-C(2)) are essentially identical with the symmetrical norbornadiene and cyclooctadiene complexes[28,29] and an ethylene complex[32] (see Table XIII). For these latter complexes the C=C bond distances are slightly shorter, but this may possibly be associated with the foreshortening of C=C separations owing to the effects of thermal motion and bonding electron density[35] in these less extensive data sets collected at room temperature. Steric crowding is probably responsible not only for the longer distance but also for the increased asymmetry in the third pair of Ru-C$_{\text{olefin}}$ distances, Ru-C(8) and Ru-C(9). Furthermore, there is also a correlation between the M-C olefin separations and the extent to which the olefinic hydrogen atoms are displaced from the C—C=C—C plane (see Table XIV).[20] Longer Ru-C$_{\text{olefin}}$ separations than those observed here are known (see Table XIII), but these are also complexes of distinctive geometry and at least a part of the lengthening may be attributed to the trans influence of carbonyl ligands competing for π-electron density. The C=C bond length, C(8)-C(9), observed for this third olefinic moiety in **1** is significantly shorter than the other two C=C separations.

In a rhodium(I) dionato complex with a substituted norbornadiene ligand an apparently similar correlation between M—C and C=C separations was reported,[36] but its significance may have been exaggerated because of conjugation effects: the long C=C and short Ru—C separations were associated with the olefin which had two carboethoxy substituents.

Coordination of the norbornadiene molecule to the metal not only lengthens the C=C bond and pushes the olefinic hydrogen atoms away from the metal but also alters the conformation of the norbornadiene ligand. In the free molecule, the dihedral angle between the two C—C=C—C planes is 115 (2)°.[37] (See Table XIV[20] for definition of these planes.) Upon coordination this decreases to 104.5°. In other words, the two olefinic groups move toward each other.

The Ru-Cl and Ru-C Separations. As may be seen from Table XIII and reviewed elsewhere,[32] mutually trans-directed chloro ligands typically have Ru-Cl bond lengths in the range 2.391 (2)[38]

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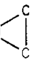
Table **XIII**. Coordination Number and Selected Bond Distances (Å) for Selected Ruthenium Complexes

compd[a]	CN[b]		C=C	Ru–C_{sp^3}	Ru–Cl
$[RuH(CH_2R)(P)_4]_2$[d]	6			2.203 (6)	
				2.219 (6)	
$Ru(Cp)(CO)_2(CHR_2)$[e]	6			2.180 (2)	
$RuCl(C_7H_8C_7H_9)(C_7H_8)$[f]	5	2.110 (2), 2.140 (2)	1.422 (2)	2.099 (2)	2.4831 (8)
		2.176 (2), 2.196 (2)	1.400 (2)		
		2.245 (2), 2.353 (2)	1.385 (2)		
$Ru[C(R)=CR_2]_2(P)(CO)_2(C=C)$[g]	6	2.32 (2), 2.48 (2)	1.37 (2)		
$Ru_2(CO)_5(C=C)_2(C_3)(CHR_2)$[h]	6	2.43 (1), 2.54 (1)	1.41 (2)	2.15 (1)	
		2.37 (1), 2.29 (1)	1.41 (2)		
Ru *trans*-$(Cl)_2(N)_2(C_7H_8)$[i]	6	2.182 (2), 2.188 (2)	1.389 (3)		2.4200 (4)
		2.182 (2), 2.189 (2)	1.388 (3)		2.4263 (4)
Ru *trans*-$(Cl)_2(N)_2(C_7H_8)$[j]	6	2.177 (4), 2.181 (4)[c]	1.385 (6)		2.407 (1), 2.415 (2)
Ru *cis*-$(Cl)_2(N)_2(COD)$[i]	6	2.177 (6), 2.180 (4)[c]	1.389 (6)		2.458 (1)
Ru *cis*-$(Cl)_2(CO)(P)_2(C_2H_4)$[k]	6	2.214 (4)[c]	1.376 (10)		2.415 (2), 2.454 (3)

[a] Only the general ligand type is given: COD, 1,5-cyclooctadiene; Cp, cyclopentadienyl; C_7H_8, norbornadiene. [b] Coordination number. [c] Molecule has crystallographically imposed geometry. [d] Reference 7b. [e] Reference 33. [f] This work. [g] Reference 30. [h] Reference 31. [i] Reference 29. [j] Reference 28. [k] Reference 32.

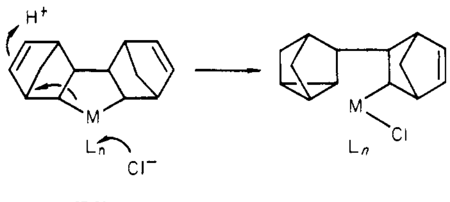
–2.446 (7) Å.[39] With the Ru–Cl separation being 2.454 (3) Å for a chloro group trans to a carbonyl ligand[32] and 2.513 (7) Å for one trans to a phosphine,[39] the trans influence of an alkyl group appears to be intermediate since the Ru–Cl separation observed for **1** is 2.483 (1) Å. Furthermore, this is consistent with the value of 239 cm^{-1} for the Ru–Cl stretching frequency, which is at lower energy than in carbonyl systems and at greater energy than the lower bound for phosphine systems.[32,40] Whereas we note that in the carbonyl- and phosphine–chloro systems the ligands are closely trans to each other, here the Cl–Ru–C angle is 148.04 (4) Å.

Although structurally characterized compounds featuring an Ru–C_{sp^3} bond are rare, the Ru–C separation observed here is more than 0.05 Å shorter than any other reported Ru–C_{sp^3} bond (see Table XIII). However, Ru–C_{sp^2} single bonds as short as 1.91 (2)[30] and as long as 2.18 (2) Å[30] have been observed.

Mechanism of Formation. Reduction of $[RuCl_2(\text{cyclic diene})]_n$ with Grignard reagents[41,42] and trichlorotriaquoruthenium(III) with zinc in ethanol[43] are reported to yield ruthenium(0) complexes, and in the latter case a (cyclic diene)(cyclic triene)Ru species results from the dehydrogenation of a cyclic diene ligand. This dehydrogenation is not possible for NBD where dehydrogenation of the allylic C–H bonds would violate Bredt's rule[44] and give highly strained tricyclo[2.2.1.0] skeletons. As a consequence, carbon–carbon bond formation occurs between two coordinated NBD molecules.

The coupling of norbornadiene derivatives via metallocycloalkyl intermediates has been observed previously for cobalt,[45] iron,[46] iridium,[47] and rhodium[48] systems. The formation of metallocyclopentanes from the oxidative cyclization of low-valent transition-metal complexes with two olefin molecules has been extensively studied for Co,[45,49] Ti,[50] Zr,[51] Ta and Nb,[52] Fe,[53] Ir,[47] Ni,[54-56] and Pt.[57,58] However, for those metallocyclopentane derivatives arising from the coupling of two NBD molecules, only the sterically more favorable exo–trans–exo configuration has been reported to date.[47] This is not consistent with the endo–endo C–C bond formation observed for **1b** and almost certainly for **1a** as well (see below). Furthermore, attempted protonation of the reaction mixture with hydrogen chloride, following the reduction of $[RuCl_2(NBD)]_n$ by zinc in acetonitrile or tetrahydrofuran, did not yield complex **1** at all. Therefore, the mechanism via a ruthenium–cyclopentane intermediate, as shown in Scheme I, was discarded. Other metallocycle derivatives, such as have been inferred for some systems,[48] are therefore also unlikely.

Scheme I



An alternative more viable mechanism for the formation of either **1a** or **1b**, and, in particular, the stereospecific formation of a carbon–carbon bond between the C(14) and C(15) carbon atoms involves a ruthenium(II) hydride intermediate, $RuHCl(NBD)_2$, generated by zinc reduction followed by protonation by the alumina. When alumina was eliminated in the preparation of **1**, the yield decreased to only 20%. On the other hand, the yield of **1** increased to 76% when ammonium chloride was employed as the proton source and ethanol as the reaction medium, although

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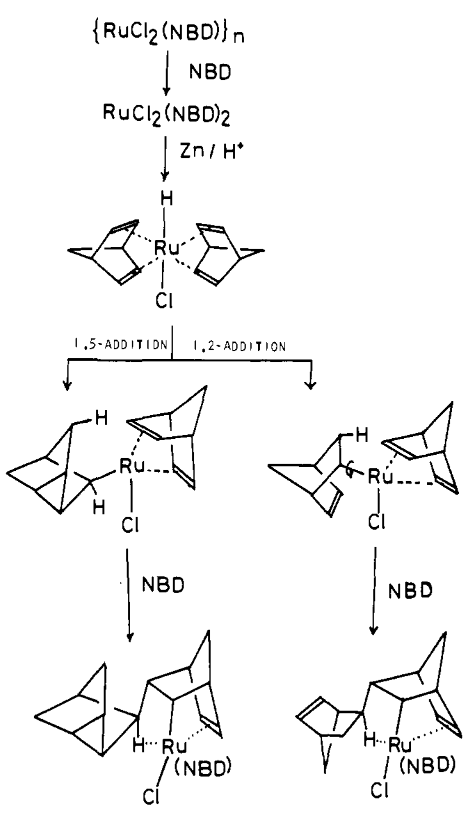
Scheme II



1a 1b

selectivity in the formation of the major isomer **1a** decreased (**1a**:**1b** = 71:29). The hydride intermediate is further supported by the fact that sodium borohydride in ethanol may also be used as a reducing agent although the yield of **1** dropped to 20% because of the over reduction of the ruthenium system.

For both isomers, formation of the C(14)–C(15) bond occurs by endo addition with respect to atom C(14) of the norbornene skeleton (ring B). The stereochemistry of the C(15) atom in the minor isomer **1b** in ring C is also endo, whereas that in the major isomer **1a** can be explained in terms of either endo or exo addition because the methylene carbon atoms C(18) and C(20) are chemically equivalent owing to the symmetry of the nortricyclane ring. However, the formation of a cyclopropane ring from norbornadiene and a second olefin under homogeneous cobalt-catalyzed cycloaddition has been explained in terms of endo addition.[44,49] In other words, formation of the nortricyclane skeleton is possible only from a bidentate NBD molecule. This is supported by our observation that excess NBD induces a dramatic decrease in the yield of **1** because bidentate coordination of one NBD molecule changes to monodentate coordination of two NBD molecules which may be coordinated from the exo side. Therefore, we believe that both isomers form the C(14)–C(15) carbon bonds in an endo–endo manner from an $RuHCl(NBD)_2$ intermediate of common structure.

A plausible mechanism for the formation of **1a** and **1b** is shown in Scheme II. The Ru–H bond of this intermediate, generated by zinc reduction followed by protonation, adds to a coordinated, bidentate NBD molecule via either 1,5-addition to give an *endo*-nortricyclyl ruthenium moiety, or via a 1,2-addition to give an *endo*-3-norbornenyl ruthenium skeleton. This process determines the structure of the ring C for both isomers. The ruthenium–carbon σ bond so generated inserts into the second bidentate NBD ligand from the endo side to finalize ring B with the formation of a ruthenium carbon σ bond at the C(13) atom.

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Supplementary Material Available: Table III of structure amplitudes, Tables IV and V of intermolecular separations, Tables VIII and IX of bond distances and angles involving hydrogen atoms, and Table XIV of least-squares planes (28 pages). Ordering information is given on any current masthead page.