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THE CRYSTAL STRUCTURE OF DICHLOROBIS(TRIPHENYLPHOSPHINE)(NORBORNADIENE)RUTHENIUM

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Summary

Passing norbornadiene in Ar over a solution of $RuCl_2[P(C_6H_5)_3]_4$ in CH_2Cl_2 results in slow deposition of single crystals of the extremely insoluble title compound. The compound crystallizes in monoclinic space group $P2_1/c$ with unit cell constants a 14.213(3), b 14.486(2), c 17.079(2) Å, β 97.13(1)°, and ρ_c 1.50 g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement has led to a final R_1 value of 0.057 based on 2460 independent observed ($I \geqslant 3\sigma(I)$) reflections. The molecule attains an approximately octahedral geometry with *cis*-chlorine and *trans*-phosphine ligands. The norbornadiene ligand bonds symmetrically to the metal with long C=C bonds of 1.408(12) and 1.415(12) Å. The average values of some other important bond distances are: Ru—Cl 2.440 ± 0.006 Å; Ru—P 2.479 ± 0.003 Å; Ru—C 2.21 ± 0.02 Å.

Introduction

Triphenylphosphine (L) complexes of ruthenium(II) have a demonstrated catalytic activity toward the hydrogenation of olefins [1]. The chloro compounds $RuCl_2L_3$ and $RuCl_2L_4$ are often introduced as catalytic precursors, although kinetic studies indicate that the active species may be $HRuClL_3$ [2]. Structural studies on $RuCl_2L_3$ and $RuCl_2L_4$ have indicated the following: (1) The solid-state structure of $RuCl_2L_3$ is best described as a distorted square pyramid with *trans* basal Cl ligands, *trans* basal L ligands, and an apical L ligand [3]. (2) The solution structure of $RuCl_2L_4$ in $CHCl_3$ shows it to be $RuCl_2L_3$ + L [4], i.e., one triphenylphosphine ligand dissociates completely, although with smaller phosphine ligands a *trans* octahedral geometry of the tetrakis-phosphine derivative has been seen [5]. Somewhat surprisingly, no structural studies of olefin adducts of $RuCl_2L_3$ and $RuCl_2L_4$ have been reported and the stereochemical consequences of olefin addition to these complexes are not known. Therefore we report herein the solid state structure of (nbd)-

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$RuCl_2L_2$ (nbd ≡ bicyclo[2.2.1]hepta-2,5-diene), a diolefin complex first prepared by Robinson and Wilkinson [6].

Experimental

The solution reaction of norbornadiene with $RuCl_2L_3$ or $RuCl_2L_4$ produces a yellow-orange insoluble product which analyzes as (nbd)$RuCl_2L_2$. This compound is so insoluble that it has not yet been studied by solution NMR [7]. It was thus apparent that recrystallization of the product would probably be impracticable and we have instead employed a novel method to obtain single crystals suitable for crystallographic analysis. Norbornadiene vapor in Ar was slowly passed over a CH_2Cl_2 solution of $RuCl_2L_4$. Over a period of several days, small yellow-orange crystals of air-stable (nbd)$RuCl_2L_2$ were deposited. A rectangular prism (approximate dimensions 0.2 × 0.2 × 0.1 mm) with well-defined faces was mounted with epoxy cement on the end of a glass fiber and used for the present study.

Data collection and structure refinement

Diffraction data were collected on an Enraf-Nonius CAD-4F autodiffractometer using Mo-K_α (λ 0.71073 Å) radiation with a graphite crystal monochromator in the incident beam. Final unit cell parameters were determined from a least-squares fit of 25 reflections in the range $28° < 2\theta < 32°$. The crystallographic and data collection parameters are summarized in Table 1. The 2466 observed data ($I \geqslant 3\sigma(I)$) were corrected for Lorentz and polarization effects but not absorption.

The position of the Ru atom was obtained via direct methods. The remainder of the structure was determined and successfully refined using Fourier and full-matrix least squares techniques *. No attempt was made to locate the hydrogen atoms, although their probable locations were calculated after refinement. The carbon atoms of the phenyl rings were refined with isotropic thermal parameters while the remaining atoms were refined with anisotropic thermal parameters. The final unweighted and weighted discrepancy indices were: $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.057$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.071$.

The final difference Fourier map showed no significant residual electron density. The positions of hydrogen atoms on the phenyl rings were calculated, but not refined, assuming a C—H bond length of 0.95 Å and idealized trigonal symmetry at the carbon atoms. The final values of the positional parameters are given in Table 2. Thermal parameters, and observed and calculated structure factor amplitudes are available as supplementary material **.

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[*] All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package including local modifications. For details pertaining to scattering factors, weighting scheme, etc., see, for example ref. 8.

[**] See NAPS Document No. 03723 for 12 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only. $5.00 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3 for photocopy and $ 1 for microfiche.

TABLE 1

CRYSTAL DATA AND ENRAF-NONIUS CAD-4 DATA COLLECTION PROCEDURES FOR $(nbd)RuCl_2L_2$

Formula	$RuCl_2P_2C_{43}H_{38}$
M	788.71
Space group	$P2_1/c$
A (Å)	14.214(3)
b (Å)	14.486(2)
c (Å)	17.079(2)
β (°)	97.13(1)
V ($Å^3$)	3489(1)
Z	4
ρ_c (g cm^{-3})	1.50
μ(Mo-K_α) (cm^{-1})	7.171
Radiation	Graphite monochromated Mo-K_α
Scan type	$\omega - 2\theta$
Scan width (°)	$0.60 + 0.35 \tan \theta$
Aperture width (mm)	$1.50 + \tan \theta$
Prescan limit	0.5σ
Max. scan speed (° min^{-1})	20.12
Max. counting time (s)	30
Collection range	$+h, +k, +l; 1° < \theta \leqslant 22.5°$
Unique data	4516
Unique data with $I \geqslant 3\sigma(I)$	2460
X-ray exposure time (h)	37
P	0.05
Crystal decomposition	Negligible
Number of variables	253
Esd	1.677
R_1	0.057
R_2	0.071
Largest shift	0.0003
Largest peak in final difference map (e $Å^{-3}$)	0.33

Results and discussion

The structure of $(nbd)RuCl_2L_2$ (I) is shown in Fig. 1, along with the labeling scheme used for the atoms. Interatomic distances and angles are presented in Tables 3 and 4, respectively. The geometry of the coordination sphere is best described as distorted octahedral in which two vertices are occupied by the double bonds of the norbornadiene ligand. The Cl atoms are *cis* to one another, but the Cl—Ru—Cl angle, 105.9(1)°, is large. It is likely that the distortion from 90° is at least partly due to repulsion of the Cl atoms by an *ortho*-hydrogen atom of one of the phenyl rings (vide infra). The triphenylphosphine ligands are most nearly *trans* to one another, although the P—Ru—P angle, 153.8(1)°, is considerably distorted from 180°. The norbornadiene ligand attains a symmetric conformation in which the double bonds are approximately *trans* to the Cl atoms. The C=C bonds of the coordinated nbd are lengthened by ca. 0.06 Å relative to the free ligand [9].

When hydrogen atom positions were calculated (assuming a C—H bond length of 0.95 Å) it was found that one of the phenyl ring *ortho*-hydrogen atoms was approximately equidistant from the two Cl atoms (Cl(1) to H 2.78 Å; Cl(2) to H 2.60 Å). The sum of the Van der Waals radii of H and Cl is 3.0 Å; hence

TABLE 2

POSITIONAL PARAMETERS FOR (nbd)RuCl$_2$L$_2$ (Estimated standard deviations in the least significant digits are shown in parentheses.)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0,22086(7)	0,50518(7)	0,28891(5)	C(131)	0,1923(8)	0,7297(8)	0,1893(6)
Cl(1)	0,1865(2)	0,4970(2)	0,1452(1)	C(132)	0,1515(9)	0,8174(9)	0,1742(7)
Cl(2)	0,3620(2)	0,6009(2)	0,3152(2)	C(133)	0,1897(9)	0,8809(9)	0,1252(7)
P(1)	0,1370(2)	0,6525(2)	0,2556(2)	C(134)	0,2708(9)	0,8558(9)	0,0913(7)
P(2)	0,3439(2)	0,3869(2)	0,2747(2)	C(135)	0,3146(9)	0.7699(9)	0,1061(7)
C(1)	0,0758(8)	0,4978(9)	0,3889(6)	C(136)	0,2747(8)	0,7067(8)	0,1577(7)
C(2)	0,0776(8)	0,4574(8)	0,3042(7)	C(211)	0,4035(8)	0,3427(8)	0,3689(7)
C(3)	0,1384(8)	0,3804(8)	0,3148(7)	C(212)	0,4707(9)	0,4001(9(	0,4142(7)
C(4)	0,1727(9)	0,3742(8)	0,4051(7)	C(213)	0,5101(9)	0,3697(9)	0,4898(7)
C(5)	0,2385(8)	0,4620(8)	0,4133(7)	C(214)	0,4835(9)	0,2887(10)	0,5203(7)
C(6)	0,1784(8)	0,5401(9)	0,4048(6)	C(215)	0,4169(9)	0,2101(9)	0,4762(8)
C(7)	0,0844(8)	0,4074(8)	0,4403(7)	C(216)	0,3774(9)	0,2594(9)	0,3997(7)
C(111)	0,0179(8)	0,6392(8)	0,2C05(6)	C(221)	0,4441(8)	0.4268(8)	0,2223(7)
C(112)	−0,0613(9)	0,6187(8)	0,2303(7)	C(222)	0,4245(9)	0,4854(9)	0,1586(7)
C(113)	−0.1497(9)	0,6029(9)	0.1956(7)	C(223)	0.4981(10)	0.5091(10)	0,1115(8)
C(114)	−0.1610(10)	0.6099(10)	0,1115(8)	C(224)	0.5893(10)	0.4707(10)	0,1315(8)
C(115)	−0,0822(9)	0,6344(9)	0,0765(7)	C(225)	0,6062(11)	0.4093(11)	0,1965(8)
C(116)	0,0068(8)	0,6485(8)	0.1188(6)	C(226)	0,5324(9)	0.3872(9)	0,2422(7)
C(121)	0,12391(8)	0,7393(8)	0,3349(6)	C(231)	0,3151(8)	0.2800(8)	0,2181(6)
C(122)	0,0377(9)	0,7833(9)	0,3429(7)	C(232)	0,2331(8)	0,2755(8)	0,1640(7)
C(123)	0,0377(10)	0.8564(10)	0.3974(8)	C(233)	0,2165(9)	0.1962(9)	0,1148(7)
C(124)	0.1221(10)	0,8819(9)	0.4438(8)	C(234)	0,2835(9)	0.1249(8)	0,1215(7)
C(125)	0,2068(9)	0,8335(9)	0,4373(7)	C(235)	0,3653(10)	0,1286(9)	0,1749(8)
C(126)	0,2001(9)	0.7632(9)	0.3817(7)	C(236)	0.3828(9)	0,2074(9)	0,2226(7)

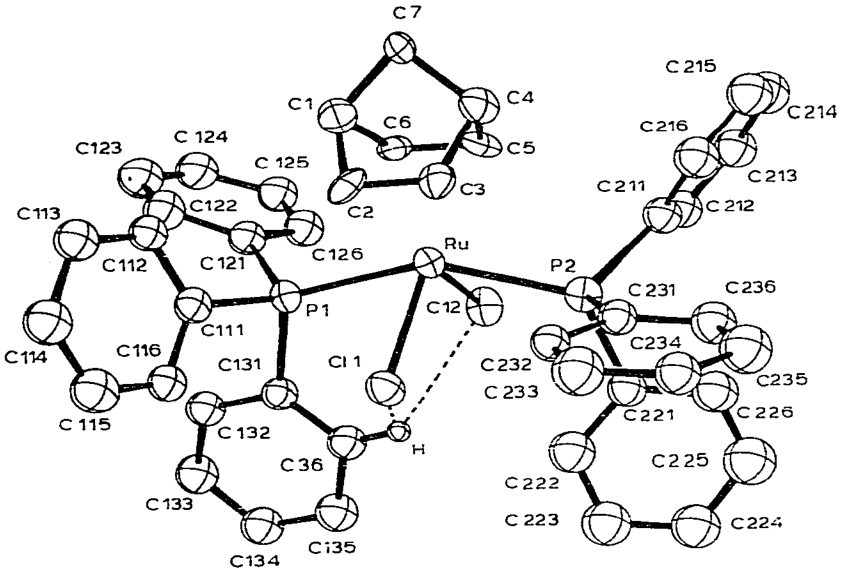


Fig. 1. Molecular structure of (nbd)$RuCl_2L_2$ drawn with 50% probability vibrational ellipsoids.

there appears to be a repulsive interaction between the H atom and the two Cl atoms, which is at least partly, and perhaps mainly, responsible for the large Cl—Ru—Cl angle.

The geometry of I represents a departure from the distorted square pyramidal geometry of $RuCl_2L_3$ (II) [3]. In II the Cl ligands occupy *trans* basal positions in the coordination sphere, with a Cl—Ru—Cl angle of 157°, much larger than that observed in I. By contrast, the P(basal)—Ru—P(basal) angle in II is 156°,

TABLE 3

BOND LENGTHS FOR (nbd)$RuCl_2L_2$ IN Å [a]

Atoms	Distance	Atoms	Distance
Ru—Cl(1)	2.446(2)	C(1)—C(2)	1.56(1)
Ru—Cl(2)	2.434(3)	C(1)—C(6)	1.57(1)
Ru—P(1)	2.476(3)	C(1)—C(7)	1.57(1)
Ru—P(2)	2.481(3)	C(4)—C(3)	1.56(1)
Ru—C(2)	2.196(9)	C(4)—C(5)	1.57(1)
Ru—C(3)	2.228(9)	C(4)—C(7)	1.53(1)
Ru—C(5)	2.199(8)	C(2)—C(3)	1.41(1)
Ru—C(6)	2.198(9)	C(5)—C(6)	1.41(1)
P(1)—C(111)	1.842(9)		
P(1)—C(121)	1.775(9)	H^b—C(136)	0.95
P(1)—C(131)	1.836(9)	H^b···Cl(1)	2.78
P(2)—C(211)	1.838(9)	H^b···Cl(2)	2.60
P(2)—C(221)	1.866(10)		
P(2)—C(231)	1.844(9)		

[a] Phenyl ring C—C distances ranged from 1.36(1) to 1.44(1) Å with a mean value of 1.40 Å. [b] Hydrogen atom position was calculated but not refined.

TABLE 4

BOND ANGLES FOR (nbd)$RuCl_2L_2$ IN DEGREES

Atoms	Angle	Atoms	Angle
Cl(1)—Ru—Cl(2)	105.9(1)	C(221)—P(2)—C(231)	98.1(4)
Cl(1)—Ru—P(1)	77.2(1)	C(2)—C(1)—C(6)	100.6(7)
Cl(1)—Ru—P(2)	85.9(1)	C(2)—C(1)—C(7)	101.3(8)
Cl(1)—Ru—C(2)	91.5(3)	C(6)—C(1)—C(7)	102.8(7)
Cl(1)—Ru—C(3)	96.5(3)	C(1)—C(2)—Ru	96.6(5)
Cl(1)—Ru—C(5)	160.1(3)	C(1)—C(2)—C(3)	104.9(8)
Cl(1)—Ru—C(6)	150.4(2)	Ru—C(2)—C(3)	72.7(5)
Cl(2)—Ru—P(1)	85.0(1)	C(2)—C(3)—Ru	70.2(5)
Cl(2)—Ru—P(2)	80.6(1)	C(2)—C(3)—C(5)	106.5(8)
Cl(2)—Ru—C(2)	155.9(3)	Ru—C(3)—C(4)	97.8(6)
Cl(2)—Ru—C(3)	150.1(3)	C(3)—C(4)—C(5)	98.7(7)
Cl(2)—Ru—C(5)	89.5(3)	C(3)—C(4)—C(7)	101.4(7)
Cl(2)—Ru—C(6)	90.9(3)	C(5)—C(4)—C(7)	102.6(8)
P(1)—Ru—P(2)	153.8(1)	C(4)—C(5)—Ru	98.6(5)
P(1)—Ru—C(2)	82.7(3)	C(4)—C(5)—C(6)	107.0(8)
P(1)—Ru—C(4)	119.6(3)	Ru—C(5)—C(6)	71.2(5)
P(1)—Ru—C(5)	117.5(3)	C(5)—C(6)—Ru	71.3(5)
P(1)—Ru—C(6)	80.2(3)	C(5)—C(6)—C(1)	103.9(8)
P(2)—Ru—C(2)	118.0(3)	Ru—C(6)—C(1)	96.2(5)
P(2)—Ru—C(3)	81.6(3)	C(1)—C(7)—C(4)	93.1(7)
P(2)—Ru—C(5)	84.3(3)	P(1)—C(111)—C(112)	120.8(7)
P(2)—Ru—C(6)	121.5(3)	P(1)—C(111)—C(116)	119.0(7)
C(2)—Ru—C(3)	37.1(3)	P(1)—C(121)—C(122)1	122.8(7)
C(2)—Ru—C(5)	78.0(4)	P(1)—C(121)—C(126)	115.1(8)
C(2)—Ru—C(6)	66.6(3)	P(1)—C(131)—C(132)	117.7(8)
C(3)—Ru—C(5)	65.0(3)	P(1)—C(131)—C(136)	122.7(7)
C(3)—Ru—C(6)	78.3(4)	P(2)—C(211)—C(212)	118.6(7)
C(5)—Ru—C(6)	37.6(3)	P(2)—C(211)—C(216)	121.4(6)
Ru—P(1)—C(111)	114.3(3)	P(2)—C(221)—C(222)	118.5(8)
Ru—P(1)—C(121)	120.0(3)	P(2)—C(222)—C(226)	118.5(7)
Ru—P(1)—C(131)	115.8(3)	P(2)—C(231)—C(232)	119.9(7)
C(111)—P(1)—C(121)	105.8(4)	P(2)—C(231)—C(236)	119.2(7)
C(111)—P(1)—C(131)	100.7(4)	C(136)—H^{b}—Cl(1)	114
C(121)—P(1)—C(131)	97.3(4)	C(136)—H—Cl(2)	122
Ru—P(2)—C(211)	114.2(3)	Cl(1)—H^{b}—Cl(2)	92.7
Ru—P(2)—C(221)	115.0(3)	Ru—Cl(1)—H^{b}	76.2
Ru—P(2)—C(231)	121.2(3)	Ru—Cl(2)—H^{b}	79.9
C(211)—P(2)—C(211)	103.4(4)		
C(211)—P(2)—C(231)	102.4(4)		

[a] Phenyl ring C—C—C angles ranged from 117(1) to 123(1)° with a mean value of 120°. [b] Hydrogen atom position was calculated but not refined.

insignificantly different from the P(1)—Ru—P(2) angle in I. A novel feature in the structure of II is the occupation of the vacant sixth coordination site of the Ru atom by a phenyl ring *ortho*-hydrogen atom. It has been proposed that this coordination is a consequence of the preferred geometry of the five-coordinate species, rather than the cause of it. In any case, there are no such interactions in I; the phenyl rings have pivoted away from the Ru center. A comparison of the bond lengths in I and II, shown in Table 5, indicates that both the Ru—P and Ru—Cl bonds are significantly longer in I than in II.

That the nbd ligand is acting as both a strong π^*-acceptor and π-donor of charge from and to the ruthenium(II) center is suggested by several structural

TABLE 5

A COMPARISON OF BOND LENGTHS AND ANGLES BETWEEN (nbd)$RuCl_2L_2$(I) AND $RuCl_2L_3$(II)

	I	II [a]
Bond lengths (Å)		
Ru—Cl	2.446(2)	2.387(7)
	2.434(3)	2.388(7)
Ru—P	2.476(3)	2.374(6)
	2.481(3)	2.412(6)
		2.230(8) [b]
Bond angles (°)		
Cl—Ru—Cl	105.7(1)	157.2(2)
P—Ru—P	153.8(1)	156.4(2)
		101.2(2) [b]
		101.4(2) [b]

[a] From ref. 3. [b] Length or angle involves the apical L ligand of II.

observations: (1) The Ru—P bonds in I are an average of 0.09 Å longer than the Ru—P(basal) bonds in II while the P—Ru—P angle is scarcely changed at all, suggesting that the nbd ligand competes better for back-donated charge than does a third triphenylphosphine. (2) The Cu—Cl bonds in I are an average of 0.05 Å longer than they are in II. Although this may be due in part to the apparent geometrical changes or to the interaction of the Cl atoms with the phenyl *o*-hydrogen atoms, it is likely that the nbd ligand is effectively competing with the Cl atoms as a charge donor to the Ru atom. (3) The C=C bonds of the coordinated norbornadiene in I are among the longest yet found for a coordinated norbornadiene molecule (Table 6). Were the nbd ligand acting as a π-acceptor only, one might except the degree of back-bonding to decrease with increasing metal oxidation state. The data in Table 6 offer no such simple correlation. Since donation out of the filled π-bonds in the nbd ligand will also serve the lengthen the C=C bonds, and since, as previously noted, such donation

TABLE 6

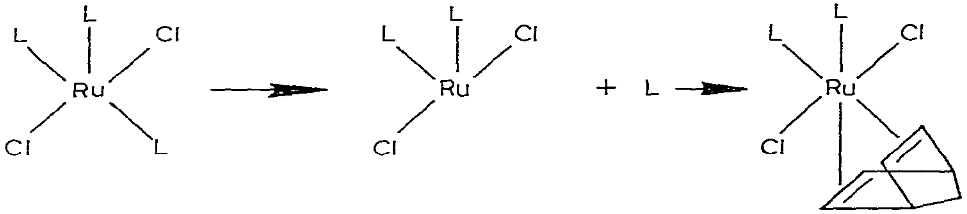
CARBON—CARBON DOUBLE BOND LENGTHS IN COORDINATED NORBORNADIENE (nbd) LIGANDS

Compound		C=C bond lengths (Å) [a]	Reference
(nbd)$PdCl_2$		1.366(9), 1.366(10)	10
$Cl_2Sn[Co(CO)_2(nbd)]_2$ [b]	nbd(1):	1.392(12), 1.388(13)	11
	nbd(2):	1.418(13), 1.385(15)	
(nbd)$Co_2(CO)_6$		1.376(7), 1.370(8)	12
(nbd)$RuCl_2(C_6H_5NH_2)_2$ [c]		1.386(6)	13
(nbd)$RuCl_2(C_5H_{11}N)_2$		1.388(3), 1.389(3)	14
$[Rh(O_2CCH_9)(nbd)]_2$ [b]	nbd(1):	1.384(5), 1.403(5)	15
	nbd(2):	1.406(5), 1.394(5)	
(nbd)$RuCl_2[P(C_6H_5)_3]_2$		1.408(12), 1.415(12)	This work
(nbd)$Mo(CO)_4$		1.400(8), 1.370(8)	16
Free nbd [d]		1.35	9

[a] Estimated standard deviations given in parentheses. [b] Two crystallographically inequivalent nbd ligands per molecule. [c] The two C=C bonds are crystallographically equivalent. [d] Electron diffraction data.

is consistent with lengthening of the Ru—Cl bonds *trans* to the C=C bonds, it seems apparent that the nbd ligand is acting as an appreciable donor of charge as well as an acceptor.

Two other compounds of general formulation $RuCl_2L_2'$(ndb) have been structurally characterized, namely those with $L' = C_6H_5NH_2$ [13] and $L' = C_5H_{11}N$ [14]. In both of these, the molecule attains a *cis*-amine, *trans*-chlorine conformation, with distortions away from octahedral symmetry similar to those found in I. Although it is reasonable to attribute the *cis*-chlorine, *trans*-phosphine geometry of I to a minimization of steric interaction between the two triphenylphosphine ligands, to do so leads to an interesting analysis of the formation of $(Nbd)RuCl_2L_2$ from $RuCl_2L_3$. First, it is noted that the axial PPh_3 in II forms P(axial)—Ru—P(basal) angles of 101°, smaller than the Cl(1)—Ru—Cl(2) angle in I. Thus, a *cis*-phosphine, *trans*-chlorine geometry for I cannot be eliminated a priori. It has been argued that second-order Jahn—Teller theory applied to a five-coordinate d^6 transition metal atom predicts a square pyramidal geometry to be favored over a trigonal-bipyramidal one [17]. Clearly the electronic constraints dominate the geometry of II, for steric arguments would seem to favor a tbp geometry with axial chlorine ligands. The crowded coordination sphere of II, and the known [4] equilibrium heavily favor a dissociative mechanism $RuCl_2L_3 \rightleftharpoons$ "$RuCl_2L_3$" + L over an associative one. If the solid-state structure of II were preserved in solution, it would be expected that a basal PPh_3 ligand would dissociate preferentially to the axial one, since the Ru—P(axial) bond is significantly (0.16 Å) shorter than the mean Ru—P-(basal) bond length. This would be expected to result in a *trans*-chlorine, *cis*-phosphine geometry of $(nbd)RuCl_2L_2$:



Caulton has demonstrated that $RuCl_2L_3$ is fluxional [4], however, presumably through a tbp transition state. If dissociation occurs from this higher energy transition state, only small structural changes would be needed to attain the observed geometry of I.

There is no reason to expect that the ligand-induced structural changes observed here would not occur for coordination of any olefin to $RuCl_2L_n$ complexes, underscoring the importance of considering substrate electronic effects when correlating the structure and reactivity of ruthenium(II) hydrogenation catalysts.

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References

1 B.R. James, Advan. Organometal. Chem., 17 (1979) 319, and ref, therein.
2 P.S. Hallman, B.R. McGarvey and G. Wilkinson, J. Chem. Soc. A, (1968) 3143.
3 S.J. LaPlaca and J.A. Ibers, Inorg. Chem., 6 (1965) 778.
4 K.G. Caulton, J. Amer. Chem. Soc., 96 (1974) 3005; P.R. Hoffman and K.G. Caulton, J. Amer. Chem. Soc., 97 (1975) 4221.
5 F.A. Cotton, B.A. Frenz and D.L. Hunter, Inorg. Chim. Acta, 16 (1976) 203.
6 S.D. Robinson and G. Wilkinson, J. Chem. Soc. A, (1966) 300.
7 L. Ruiz-Ramirez, T.A. Stephenson and E.S. Switkes, J. Chem. Soc. Dalton Trans., (1973) 1770.
8 F.A. Cotton, W.H. Ilsley and W. Kaim, Inorg. Chem., 19 (1980) 1450.
9 A. Yokozeki and K. Kuchitsu, Bull. Chem. Soc. Japan, 44 (1971) 2356.
10 N.C. Baenziger, G.F. Richards and J.R. Doyle, Acta Crystallogr., 18 (1965) 924.
11 F.P. Boer and J.J. Flynn, J. Amer. Chem. Soc., 93 (1971) 6495.
12 F.S. Stephens, J. Chem. Soc. A, (1972) 1754.
13 J.-M. Manoli, A.P. Gaughan, Jr. and J.A. Ibers, J. Organometal. Chem., 72 (1974) 247.
14 C. Potvin, J.M. Manoli, G. Pannetier, R. Chevalier and N. Platzer, J. Organometal. Chem., 113 (1976) 273.
15 A.H. Reis, Jr., C. Willi, S. Siegel and B. Tani, Inorg. Chem., 18 (1979) 1859.
16 J.L. Atwood, D.J. Darensbourg and R. Shakir, personal communication.
17 R.G. Pearson, J. Amer. Chem. Soc., 91 (1969) 4947.