

Synthesis, Structure, and Stereochemistry of Five-Coordinate Platinum(II)-Olefin Complexes with a Chiral Diamine¹

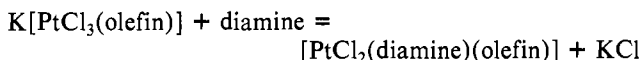
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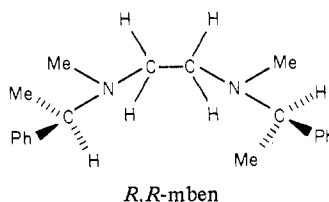
New five-coordinate platinum(II) complexes of general formula $[\text{PtCl}_2(\text{diamine})(\text{olefin})]$, where diamine = (*R,R*)-*N,N'*-dimethyl-*N,N'*-bis(α -methylbenzyl)-1,2-ethanediamine (*R,R*-mben) and olefin = acrolein (AA), acrylonitrile (AN), fumarodinitrile (FN), maleic anhydride (MA), and maleimide (MI) were prepared and characterized. The crystal structures of the already known ethene (**1**) and propene (**2**) complexes have been determined by X-ray diffraction studies. Both compounds crystallize in the tetragonal space group $P4_32_12$ with four molecules per unit cell. Lattice parameters (25 °C) are $a = b = 13.016$ (3) Å, $c = 13.719$ (4) Å and $a = b = 13.180$ (2) Å, $c = 13.850$ (2) Å for complexes **1** and **2**, respectively. The whole geometry corresponds to a trigonal bipyramid with the chlorine atoms in the axial positions. The olefin and the diamine ligand lie in the equatorial plane. The two prochiral nitrogen atoms have equal absolute configurations identical with that of the asymmetric carbon atoms of *R,R*-mben. ¹H NMR spectra are reported and discussed in order to get information on the rotation of the olefinic ligand and other stereochemical features of the complexes.

Introduction

Recently we have reported² on the facile synthesis of several isolable five-coordinate complexes of general formula $[\text{PtCl}_2(\text{diamine})(\text{olefin})]$, by reaction of a diamine with a Zeise-type anion:



The diamine ligand was an *N,N'*-substituted 1,2-ethanediamine. The unsaturated ligand was either ethene or a higher olefin. Generally these complexes lose the olefin^{2,3} on standing in solution, affording four-coordinate species of the type $[\text{PtCl}_2(\text{diamine})]$. The decomposition mechanism is solvent dependent,⁴ and its rate appears to be related² to the electronic and steric features of the diamine. Among the already² described compounds, the chiral diamine (*R,R*)-*N,N'*-dimethyl-*N,N'*-bis(α -methylbenzyl)-1,2-ethanediamine (henceforth called *R,R*-mben) appears to confer the highest stability and/or inertness toward this decomposition.



The well-known interest⁵ in five-coordination in the chemistry of d^8 ions prompted us to extend our study to the preparation of other five-coordinate olefin complexes containing *R,R*-mben and to the structural investigation of this class of compounds.

We report here the synthesis of complexes with the substituted olefins acrolein (AA), acrylonitrile (AN), fumarodinitrile (FN), maleic anhydride (MA), and maleimide (MI). The molecular structure of $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{R,R}\text{-mben})]$ and

$[\text{PtCl}_2(\text{CH}_3\text{CH}=\text{CH}_2)(\text{R,R}\text{-mben})]$, determined by X-ray diffraction, are described. Stereochemical features of the complexes, related to the configuration of the coordinated diamine and/or of the olefinic ligand, are discussed.

Experimental Section

Microanalyses were performed by Analytische Laboratorien, Elbach, West Germany. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in Nujol mulls. ¹H NMR spectra were recorded on Varian T-60A and Bruker WH 270 spectrometers in CDCl_3 solution with the use of Me_4Si as internal standard. All solvents and chemicals were of AR grade purity.

The complexes $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{R,R}\text{-mben})]$ (**1**) and $[\text{PtCl}_2(\text{CH}_3\text{CH}=\text{CH}_2)(\text{R,R}\text{-mben})]$ (**2**) were prepared as reported.² A sample of *R,S*-mben was synthesized with Caspe's procedure⁶ from (*S*)-*N,N'*-dimethylbenzenemethanamine and (*R*)-*N,N'*-dimethyl-*N*-(2-bromoethyl)benzenemethanamine, which was obtained with Cortese's method⁷ from (*R*)-*N,N'*-dimethyl-*N*-(2-hydroxyethyl)benzenemethanamine. This latter compound was prepared following the method of Samdhal and Weider⁸ from (*R*)-*N,N'*-dimethylbenzenemethanamine and 2-bromoethanol.

Preparation of $[\text{PtCl}_2(\text{R,R}\text{-mben})(\text{olefin})]$ Complexes: Olefin = AA (**3**), AN (**4**), FN (**5**), MA (**6**), MI (**7**). To a solution of 0.59 g (1 mmol) of complex **1** in 15 mL of benzene was added an excess of the appropriate olefinic ligand at room temperature with stirring. In the case of FN, complex **5** precipitated within 30 min as yellow well-formed crystals. In all other cases, the mixture was evaporated to dryness after 24 h and the residue was crystallized from dichloromethane-methanol or acetone-cyclohexane. Complex **7** could not be recrystallized, owing to a very poor solubility in common organic solvents. All complexes were in the form of yellow to yellow-orange crystalline solids and were obtained in 70-90% yields. Analytical and ¹H NMR data are reported in Tables I and II.

Preparation of $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{R,S}\text{-mben})]$ (8**).** This compound was synthesized from Zeise's salt and *R,S*-mben by using the same procedure described² in the case of complex **1**. The title complex, which was more soluble than **1** in organic solvents, was obtained in 60% yield after recrystallization from dichloromethane-methanol; mp 98-100 °C dec. Anal. Calcd for $\text{PtCl}_2(\text{C}_2\text{H}_4)[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5]$: C, 44.74; H, 5.46; Cl, 12.01. Found: C, 44.6; H, 5.5; Cl, 12.2. The ¹H NMR spectrum in CDCl_3 showed resonances at δ 7.30 (multiplet, C_6H_5), 4.94 (quartet, CHCH_3), 3.72 (broad, C_2H_4 , $^2J(^{195}\text{Pt}-\text{H}) = 70$ Hz), 2.99 and 2.28 (two multiplets, $\text{NCH}_2\text{CH}_2\text{N}$), 2.64 (singlet, NCH_3), and 1.88 (doublet, CHCH_3). When the temperature was raised, the signal attributed to the olefinic protons became a sharp singlet.

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Table I. Analytical and Characterization Data for [PtCl₂(olefin)(*R,R*-mben)] Complexes (3-7)

compd (olefin)	% calcd				% found				mol wt		mp, °C ^a	$\nu(\text{Pt-Cl})^b$ cm ⁻¹
	C	H	N	Cl	C	H	N	Cl	calcd	found		
3 (CH ₂ =CHCHO)	44.7	5.2	4.5	11.5	44.5	5.0	4.2	11.8	618.5	603	109-113	330
4 (CH ₂ =CHCN)	44.9	5.1	6.8	11.5	44.6	4.8	6.6	11.9	615.5	590	108-110	340
5 (<i>E</i> -CNCH=CHCN)	45.0	4.7	8.7	11.1	44.9	4.7	8.5	11.2	640.5	636	130-132	340
6 (OCCH=CHCO)	43.6	4.6	4.3	10.7	43.2	4.5	4.0	11.0	660.5	642	131-135	340
7 (OCCH=CHCO)	43.7	4.7	5.1	10.7	43.4	4.4	4.8	11.1	659.5	^c	178-182	340

^a With decomposition. ^b In Nujol mulls. ^c Too insoluble for molecular weight determination.

Table II. ¹H NMR Data for [PtCl₂(olefin)(*R,R*-mben)] Complexes (1-7)^a

compd (olefin)	olefin protons		<i>R,R</i> -mben protons ^c			
	>C=C< ^b	others	NCH	NCH ₃	NCH ₂ CH ₂ N ^d	CCH ₃
1 (CH ₂ =CH ₂)	3.67 (AA'BB', 71)		4.88 (q)	2.63 (s)	3.06, 1.86	1.96 (d)
2 (CH ₃ CH=CH ₂)	4.57, 3.84, 3.80 (ABX ^e) 4.94, 4.04, 3.91 (ABX ^e)	1.30 (d, 52) 1.35 (d ^e)	4.81 ^f (q) 4.61 ^f (q)	2.54 ^g (b) ^j	3.15, 1.9 ^h 3.27 ^j	1.95 ⁱ (b) ^j
3 (CH ₂ =CHCHO)	4.62, 4.25, 3.90 (ABX ^e)	10.01 (d)	5.06 (q), 4.87 (q)	2.64 (s), 2.60 (s)	3.07, 1.82	1.98 (d), 1.90 (d)
4 (CH ₂ =CHCN)	4.1-3.6 ^k		5.06 (q), 5.02 (q) 5.15 (q), 4.88 (q)	2.73 ^l (s) 2.77 (s), 2.66 (s)	3.15, 1.9 ^m 3.23, 2.00	2.02 (d), 1.87 (d) 1.94 (d), 1.91 (d)
5 (<i>E</i> -CNCH=CHCN)	4.35 (A ₂ , 70)		5.15 (q)	2.80 (s)	3.15, 1.9 ^m	1.93 (d)
6 (OCCH=CHCO)	4.77 (AB, 75)		5.14 (q), 5.06 (q)	2.77 (s), 2.71 (s)	3.15, 1.9 ^h	1.97 (d), 1.91 (d)
7 (OCCH=CHCO)	4.66 (AB, 76)	1.65 (b)	5.16 (q), 5.09 (q)	2.75 (s), 2.70 (s)	3.15, 1.88	2.02 (d), 1.97 (d)

^a Spectra recorded in CDCl₃ solution at 20 °C at 270 MHz; chemical shifts are in ppm vs. Me₄Si (δ 0.00). s = singlet, d = doublet, q = quartet, b = broad signal; coupling constants $J(^{195}\text{Pt-H})$ (in Hz) are given in parentheses. ^b Figures refer to the center of gravity of multiplets. ^c Aromatic protons give a multiplet centered at δ 7.30. ^d Figures refer to the center of gravity of two multiplets constituting an AA'XX' (complexes 1 and 5) or an ABXY system (complexes 2, 3, 4, 6, and 7). ^e Coupling constants with ¹⁹⁵Pt not evaluable. ^f Two superimposed quartets. ^g When the temperature is lowered, this broad signal resolves into two sharp singlets. ^h Partially obscured by the CCH₃ signals. ⁱ When the temperature is lowered, this broad signal resolves into two sharp doublets. ^j Partially superimposed on the corresponding signals of the more abundant diastereoisomer. ^k Complex pattern of lines constituting two ABC systems. ^l Two superimposed singlets. ^m Two superimposed ABXY systems.

Preparation of [PtBr₂(C₂H₄)(*R,R*-mben)] (9). The reported² procedure for complex 1, when applied to potassium tribromo(ethene)platinate(1-) monohydrate⁹ and *R,R*-mben, gave an orange crystalline solid in 65% yield; mp 107-108 °C dec. Anal. Calcd for PtBr₂(C₂H₄)[C₆H₅CH(CH₃)N(CH₃)CH₂CH₂N(CH₃)CH(CH₃)C₆H₅]: C, 38.89; H, 4.75; Br, 23.52. Found: C, 39.1; H, 4.8; Br, 23.2. The ¹H NMR spectrum in CDCl₃ showed resonances at δ 7.30 (multiplet, C₆H₅), 5.11 (quartet, CHCH₃), 4.00 (AA'BB' multiplet, C₂H₄, ² $J(^{195}\text{Pt-H}) = 72$ Hz), 3.12 and 1.9 (two doublets, NCH₂CH₂N), 2.79 (singlet, NCH₃), and 1.92 (doublet, CHCH₃).

Preparation of [PtBr₂Cl_{2-x}(C₂H₄)(*R,R*-mben)], $x = 0, 1, 2$. A mixture¹⁰ of the three title compounds was obtained by the following procedure. Potassium trichloro(ethene)platinate(1-) monohydrate (0.38 g, 1 mmol) and potassium tribromo(ethene)platinate(1-) monohydrate (0.52 g, 1 mmol) were dissolved in 10 mL of methanol at room temperature. After 15 min of stirring, the mixture was cooled with an ice bath and *R,R*-mben (0.66 g, 2.2 mmol) was added. Suddenly a yellow solid precipitated, which was collected by filtration and dried. Recrystallization from dichloromethane-methanol gave 0.91 g of yellow-orange needles. The ¹H NMR spectrum of this material in CDCl₃ solution showed the presence of the three title complexes in the approximate ratio 2:4:1. Comparison of this spectrum

Table III. Crystal Data and Data Collection Details

	complex 1	complex 2
formula	C ₂₂ H ₃₂ Cl ₂ N ₂ Pt	C ₂₃ H ₃₄ Cl ₂ N ₂ Pt
formula wt	590.51	604.54
space group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2
<i>a</i> , Å	13.016 (3)	13.180 (2)
<i>b</i> , Å	13.016 (3)	13.180 (2)
<i>c</i> , Å	13.719 (4)	13.850 (2)
<i>V</i> , Å ³	2324.2	2405.9
<i>d</i> _{obsd} , g/cm ³	1.67	1.66
<i>d</i> _{calcd} , g/cm ³	1.69	1.67
<i>Z</i>	4	4
λ , Å	0.7107 (Mo K α)	1.5418 (Cu K α)
abs coeff, cm ⁻¹	65.88	132.68
monochromator		flat graphite crystal
takeoff angle, deg	2.0	2.0
method	ω -2 θ	ω -2 θ
scan speed, deg/min	2	4-20
stds	2 every 60 min	2 every 60 min
2 θ limit, deg	80	140
no. of data	1287	1498
no. of obsd data	789 ($I \geq 2.5\sigma(I)$)	956 ($I \geq 2.0\sigma(I)$)

with those of complexes 1 and 9 indicated that the olefinic protons in the species in which $x = 1$ give rise to a complex multiplet at δ 3.7-3.9. The other resonances were partially superimposed on the corresponding signals of complexes 1 and 9, thus preventing a precise assignment.

Preparation of [PtBr₂(FN)(*R,R*-mben)] (10). A solution of complex 9 (0.34 g, 0.5 mmol) and FN (0.078 g, 1 mmol) in benzene (10 mL) was stirred at room temperature for 2 h. Concentration of the mixture and addition of methanol gave an orange crystalline solid under refrigeration. The crystals (0.25 g, 70% yield) were collected and dried; mp 115-118 °C dec. Anal. Calcd for PtBr₂[(CN)CH=CH(CN)][C₆H₅CH(CH₃)N(CH₃)CH₂CH₂N(CH₃)CH(CH₃)C₆H₅]: C, 39.52; H, 4.15; Br, 21.91. Found: C, 39.7; H, 4.3; Br, 21.6. The ¹H NMR spectrum in CDCl₃ showed resonances at δ 7.30 (multiplet, C₆H₅), 5.43 (quartet, CHCH₃), 4.67 (singlet, (CN)CH=CH(CN)),

(9) Synthesis of potassium tribromo(ethene)platinate(1-) monohydrate was performed by shaking for 2 days an aqueous 2 M HBr solution of potassium tetrabromoplatinate(II) with ethene in the presence of a catalytic amount of tin(II) bromide. Concentration of the solution in vacuo over 18 M H₂SO₄ and KOH pellets gave large orange crystals of the product.

(10) The most straightforward procedure for synthesizing pure [PtBrCl(C₂H₄)(*R,R*-mben)] complex should involve the reaction of *R,R*-mben with potassium *ab*-dibromo-*d*-chloro-*c*-(ethene)platinate(1-) or potassium *b*-bromo-*ad*-dichloro-*c*-(ethene)platinate(1-). Actually, although these two latter compounds are claimed to be known (see M. Herberhold in "Metal π -Complexes", Vol. II, Part 1, Elsevier, Amsterdam, 1972, p 186, and references cited therein), the described procedures for their synthesis always afforded mixtures of various (ethene)trihaloplatinate(1-) anions, probably by halogen-trading reactions, as observed for other olefin complexes: F. Pesa, L. Spaulding, and M. Orchin, *J. Coord. Chem.*, 4, 225 (1975).

Table IV. Final Positional and Thermal Parameters^{a,b}

A. Complex 1 [PtCl ₂ (C ₂ H ₄)(<i>R,R</i> -mben)]									
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ² ^c	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ² ^c
Pt	0.0919 (1)	0.0919 (1)	0.0 (0)		C(5)	-0.1102 (20)	0.2523 (21)	-0.0622 (19)	6.5 (6)
Cl	0.0976 (4)	0.0959 (4)	-0.1689 (4)		C(6)	-0.2509 (12)	0.1223 (12)	-0.0953 (11)	2.8 (3)
N	-0.0891 (9)	0.0713 (10)	-0.0012 (10)	3.8 (2)	C(7)	-0.3206 (17)	0.1748 (17)	-0.0398 (17)	5.3 (5)
C(1)	0.1553 (18)	0.2387 (18)	-0.0114 (19)	6.1 (5)	C(8)	-0.4280 (23)	0.1589 (24)	-0.0636 (19)	7.1 (6)
C(2)	-0.1054 (12)	-0.0427 (13)	-0.0275 (12)	3.5 (3)	C(9)	-0.4580 (16)	0.0853 (17)	-0.1326 (12)	4.6 (4)
C(3)	-0.1349 (16)	0.0998 (14)	0.0897 (16)	4.8 (4)	C(10)	-0.3896 (21)	0.0405 (23)	-0.1850 (17)	7.1 (6)
C(4)	-0.1350 (14)	0.1423 (14)	-0.0808 (12)	3.7 (3)	C(11)	-0.2907 (14)	0.0522 (15)	-0.1684 (13)	4.0 (4)
atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$		$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$		
Pt	0.0060 (0)	0.0060 (0)	0.0048 (1)		-0.0032 (1)	0.0006 (0)	-0.0006 (0)		
Cl	0.0074 (4)	0.0085 (5)	0.0055 (4)		0.0001 (6)	0.0026 (6)	0.0018 (7)		
B. Complex 2 [PtCl ₂ (CH ₃ CH=CH ₂)(<i>R,R</i> -mben)]									
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ² ^c	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> , Å ² ^c
Pt	0.0901 (1)	0.0901 (1)	0.0 (0)		C(6)	-0.2462 (12)	0.1175 (10)	-0.1053 (14)	5.3 (4)
Cl	0.1003 (4)	0.0855 (5)	-0.1657 (5)		C(7)	-0.3195 (10)	0.1751 (11)	-0.0583 (10)	6.1 (4)
N	-0.0872 (9)	0.0710 (9)	-0.0085 (9)	5.6 (3)	C(8)	-0.4181 (22)	0.1611 (20)	-0.0669 (24)	7.9 (5)
C(1)	0.1518 (21)	0.2404 (31)	-0.0121 (22)	14.1 (10)	C(9)	-0.4547 (20)	0.0853 (21)	-0.1382 (20)	8.2 (5)
C(2)	-0.1059 (14)	-0.0359 (13)	-0.0323 (11)	5.6 (4)	C(10)	-0.3819 (22)	0.0299 (20)	-0.1840 (14)	7.6 (5)
C(3)	-0.1398 (12)	0.0986 (14)	0.0865 (13)	6.3 (4)	C(11)	-0.2810 (10)	0.0457 (12)	-0.1713 (14)	5.8 (4)
C(4)	-0.1306 (10)	0.1385 (21)	-0.0919 (14)	6.6 (4)	C(12)	0.1391 (42)	0.3071 (34)	0.0407 (35)	8.5 (12)
C(5)	-0.1068 (23)	0.2467 (22)	-0.0720 (15)	7.7 (5)					
atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$		$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$		
Pt	0.0082 (0)	0.0082 (0)	0.0141 (1)		-0.0033 (1)	-0.0006 (3)	0.0006 (3)		
Cl	0.0114 (4)	0.0146 (4)	0.0159 (4)		0.0046 (7)	0.0111 (7)	0.0119 (8)		

^a Estimated standard deviations in parentheses referring to the last digit. ^b Anisotropic temperature factors are defined by $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$. ^c Isotropic temperature factor.

²J(¹⁹⁵Pt-H) = 70 Hz), 3.2 and 2.0 (two doublets partially obscured by other lines, NCH₂CH₂N), 3.01 (singlet, NCH₃), and 1.90 (doublet, CHCH₃).

Preparation of [PtBr_xCl_{2-x}(FN)(*R,R*-mben)], *x* = 0, 1, 2. A mixture of these three complexes was obtained following the above reported procedure from FN and the corresponding mixture of ethene complexes, in 60% yield. The ¹H NMR spectrum of the product in CDCl₃ solution showed the three complexes in the approximate ratio 3:5:1. Comparison of this spectrum with those of complexes **5** and **10** allowed us to ascertain that the olefinic protons in the species in which *x* = 1 gave rise to four lines at δ 4.62, 4.58, 4.42, and 4.38, constituting an AB quartet.

X-ray Data Collection and Reduction. [PtCl₂(C₂H₄)(*R,R*-mben)] (**1**). Yellow crystals in the form of needles were grown from a 1:1 dichloromethane-methanol dilute solution. Accurate cell parameters and intensity data were obtained by using a single-crystal Siemens AED diffractometer, equipped with a PDP/I digital computer. The values of the unit cell parameters and the crystal orientation matrix were determined from a least-squares¹¹ treatment of the 2θ , ψ , and φ setting angles of 12 reflections with large 2θ values. Details of crystal data and data collection are listed in Table III. Integrated five-peak intensities were measured with the ω - 2θ scan mode with a pulse-height analyzer and a scintillation counter using Zr-filtered Mo K α radiation. A scan range of 2.0° was found to be sufficient in the range of the 2θ examined. Two half-integrated peak intensities were taken with a scanning time equal to half of the total integrated peak while the times for the two stationary-crystal, stationary-counter background counts were equal to that of the half-integrated peak. Of the total 1287 independent intensities, 789 had $I \geq 2.5\sigma(I)$ and were used in subsequent calculations. Lorentz, polarization, and absorption corrections were applied. Anomalous-dispersion corrections for atomic scattering factors were applied to the platinum atom scattering curve.¹²

[PtCl₂(CH₃CH=CH₂)(*R,R*-mben)] (**2**). Yellow crystals in the form of needles were grown from an acetone dilute solution. For this compound a CAD-4 Enraf-Nonius diffractometer equipped with PDP8/M and PDP11/34 digital computers was used for data collection and refinement. Unit cell parameters and the orientation matrix were obtained from a least-squares treatment of the angular settings

of 25 carefully centered high- θ reflections.¹³ Details of crystal data and data collection are given in Table III. The standard deviations of the lattice parameters were determined by comparison of the deviations from integer values of the indices, calculated with the orientation matrix, for the angular settings of the orientation reflections as described by Duisenberg.¹⁴ Intensity data were collected in the ω - 2θ scan mode by using graphite-monochromatized Cu K α radiation. The applied scan angle was $\Delta\omega = (1.30 + 0.15 \tan \theta)^\circ$. The background was measured in an additional area of $\Delta\omega^\circ/4$ on both sides of the main scan and with the same scan speed. Prescan runs were made with a speed of 20.17°/5 min. Reflections with a net intensity $I \leq 0.5\sigma(I)$ were flagged as "weak"; those having $I > 0.5\sigma(I)$ were measured at lower speed (in the range 1-5°/min) depending on the value of $\sigma(I)/I$. The maximum time allowed for the scan was set at 60 s. Two intensity-control reflections were recorded every 60 min of X-ray exposure time: no significant change in their intensity was observed during data collection. Orientation checks were made with respect to the scattering vectors of four strong reflections every 200 reflections; reorientation was made by using 25 high-angle reflections if displacement exceeded the calculated value of 0.15°. The vertical and horizontal detector apertures were 4 mm and (3.0 + 0.5 tan θ) mm, respectively, and the distance from the crystal and the aperture was 368 mm. The tube placed between the goniometer head and the detector aperture was evacuated by using a vacuum pump. A total of 1498 reflections were collected; of these 956 having a net intensity¹⁵ greater than $2.0\sigma(I)$ were used in subsequent calculations. All reflections were corrected for Lorentz, polarization, and absorption factors. Anomalous-dispersion corrections for atomic scattering factors were applied to the Pt, Cl, C, and N atom scattering curve.^{16a,b}

Solution and Refinement of the Structure of 1. Two space groups, *P4*₁*2*₁*2* and *P4*₃*2*₁*2*, were allowed by the systematic absences *h*00 with

(11) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
 (12) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, Tables 3.3.1B and 3.3.2C.

(13) "CAD-4-Users Manual", Enraf-Nonius, Delft, 1976.
 (14) A. I. M. Duisenberg, "Collected Abstracts of the First European Enraf-Nonius CAD-4-Users Meeting", Paris, June 1974.
 (15) The net intensity was $I(\text{net}) = [s - 2(L + R)]/npi$, where $(L + R)$ is the total background count, s the scan count, and npi the ratio of the maximum possible scan speed to the applied scan speed. The standard deviation in the net intensity was calculated with $\sigma(I) = (20.1166/npi)[s + 4(L + R)]^{1/2}$. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by $\sigma(F) = (\sigma(I)/Lp)^{1/2}F_0$.
 (16) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) Table 2.3.1; (b) Table 2.2B.

Table V. Bond Lengths (Å) and Angles (deg) for Complexes 1 and 2^a

	Bond Lengths				
	complex 1	complex 2	complex 1	complex 2	
Pt-Cl	2.319 (5)	2.300 (5)	C(6)-C(7)	1.367 (27)	1.391 (19)
Pt-N	2.372 (12)	2.354 (9)	C(6)-C(11)	1.451 (24)	1.394 (19)
Pt-C(1)	2.087 (24)	2.148 (29)	C(7)-C(8)	1.450 (38)	1.318 (21)
N-C(2)	1.542 (22)	1.467 (16)	C(8)-C(9)	1.406 (35)	1.486 (23)
N-C(3)	1.431 (25)	1.531 (17)	C(9)-C(10)	1.294 (33)	1.362 (22)
N-C(4)	1.551 (22)	1.565 (16)	C(10)-C(11)	1.317 (32)	1.357 (22)
C(4)-C(5)	1.490 (33)	1.486 (24)	C(12)-C(1)		1.155 (40)
C(4)-C(6)	1.544 (24)	1.559 (21)			
Bond Angles					
	complex 1	complex 2	complex 1	complex 2	
Pt-N-C(2)	104.3 (12)	106.3 (7)	C(4)-C(6)-C(7)	119.5 (33)	121.8 (13)
Pt-N-C(3)	112.2 (17)	112.4 (7)	C(4)-C(6)-C(11)	122.9 (32)	121.4 (13)
Pt-N-C(4)	108.6 (14)	109.8 (8)	C(5)-C(4)-C(6)	113.3 (31)	113.5 (11)
Cl-Pt-N	91.6 (6)	90.3 (3)	C(6)-C(7)-C(8)	116.2 (40)	124.5 (16)
Cl-Pt-C(1)	83.8 (10)	85.7 (8)	C(6)-C(11)-C(10)	122.8 (40)	120.8 (14)
N-Pt-C(1)	119.7 (18)	118.1 (7)	C(7)-C(8)-C(9)	121.7 (44)	118.3 (17)
N-C(4)-C(5)	111.7 (29)	109.3 (13)	C(7)-C(6)-C(11)	117.6 (33)	116.7 (13)
N-C(4)-C(6)	111.5 (22)	110.1 (12)	C(8)-C(9)-C(10)	118.8 (48)	116.2 (17)
C(2)-N-C(3)	113.4 (27)	110.1 (10)	C(9)-C(10)-C(11)	122.3 (45)	123.2 (17)
C(2)-N-C(4)	110.8 (23)	108.6 (10)	C(1)-C(1')-C(12)		120.1 (34)
C(3)-N-C(4)	107.4 (25)	109.5 (9)			

^a Estimated standard deviations are in parentheses.

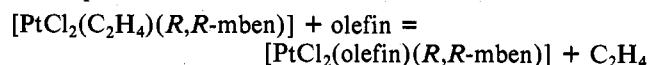
$h = 2n$ and $00l$ with $l = 4n$. The content of the unit cell ($Z = 4$; $d_{\text{calcd}} = 1.69$, $d_{\text{obsd}} = 1.67 \text{ g/cm}^3$) indicated in the molecule of complex 1 the presence of a twofold axis as a crystallographic symmetry element in the solid, so that the asymmetric unit consists of only half a molecule. The structure has been solved by a straightforward application of the heavy-atom method. The positions of the platinum and chlorine atoms were determined from the Patterson function, and the subsequent Fourier synthesis revealed the positions of the remaining lighter atoms in the independent unit. The structure was refined in the $P4_32_1$ space group corresponding to the already known absolute configuration (R) of the C(4). The refinement of the atomic parameters was carried out by means of eight cycles of a block-diagonal least-squares procedure¹⁷ (the last four cycles were performed with anisotropic thermal parameters for the two heavy atoms). The refinement continued until the maximum shifts on the atomic coordinates and the anisotropic thermal parameters were less than one-fifth and one-third of the corresponding standard deviations, respectively. The weighting scheme proposed by Cruickshank and Pilling¹⁸ was applied. At the end of the refinement the R values were $R_F = 0.050$ and $R_{wF} = 0.057$. The final coordinates and thermal factors are reported in Table IV. All calculations were carried out on a 1106 UNIVAC computer using programs written by Immirzi.¹⁹

Solution and Refinement of the Structure of 2. Examination of the unit cell dimensions and systematic absences ($h00$ with $h = 2n$ and $00l$ with $l = 4n$) indicates that complexes 1 and 2 are isomorphous. Then, the molecule in complex 2 cannot possess a twofold axis because of the presence of the coordinated propene ligand. However, since the unit cell contains four units of formula $[\text{PtCl}_2(\text{CH}_3\text{CH}=\text{CH}_2)(R,R\text{-mben})]$ ($Z = 4$; $d_{\text{calcd}} 1.67$, $d_{\text{obsd}} 1.66 \text{ g/cm}^3$), the structure should present disorder as far as the atomic positions of the propene ligand are considered. As the starting point, the same coordinates of compound 1 were used for the solution of the structure. After five least-squares cycles, the R index was 0.10. A difference Fourier map revealed the position of the C(1) and C(12) atoms, but the electron density was very broad especially in the direction of the c axis. This is reflected in the large value of the thermal parameters. Further refinement with anisotropic thermal parameters for the platinum and chlorine atoms was performed, after the introduction of weights on the basis of counting statistics, with a weight factor $w = 1/\sigma(F_o)^2$.

The refinement was ended when the maximum shifts on the atomic coordinates and thermal parameters were less than one-fifth and one-third of the corresponding standard deviations. The final R values were $R_F = 0.056$ and $R_{wF} = 0.074$. The average deviation in an observation of unit weight, defined by $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, where m is the number of observations and n the number of variables, was 1.84 as compared to the ideal value of 1. The final atomic parameters are reported in Table IV. All calculations were carried out on a PDP11/34 digital computer using the SDP package of crystallographic programs given by Enraf-Nonius (Centro di Metodologia Chimico-Fisica, Università di Napoli).

Results and Discussion

Preparation of the Complexes. The procedure used for the preparation of the complexes with the above-mentioned substituted olefins involved the exchange of the coordinated ethene in complex 1:



The reaction was carried out at room temperature in benzene solution, and the product precipitated when the mixture was allowed to stand or was concentrated. All complexes are air-stable yellow solids. All of them can be recrystallized from dichloromethane-methanol or acetone-cyclohexane, but the poorly soluble MI complex. Analytical, physical, and infrared data are listed in Table I. ¹H NMR spectra are reported in Table II.

Comparison of the ¹H NMR spectra of fresh and aged (after 24 h at room temperature) chloroform solutions indicated that the stabilities²⁰ of the complexes are similar to or possibly higher than that of the ethene complex.² Actually no appreciable change of the spectra of the aged solutions could be observed. Such changes could be detected² instead for the propene and 2-butene complexes. Thus, the presence of electron-withdrawing groups on the coordinated double bond appears to increase stability and/or inertness, while electron-donor groups exert an opposite influence. This result is in agreement with previous²¹ observations on the influence of π back-bonding on the stability of five-coordinate complexes.

(17) The function minimized was $\sum (w(|F_o| - |F_c|))^2$. The refinement was on F . The unweighted and weighted residuals are defined as follows: $R_F = \sum (|F_o| - |F_c|) / \sum |F_o|$; $R_{wF} = [(\sum w(|F_o| - |F_c|)^2) / (\sum w|F_o|^2)]^{1/2}$.

(18) D. W. I. Cruickshank and D. R. Pilling, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis", R. Pepinsky, J. M. Robertson, and J. C. Spesman, Eds., Pergamon Press, New York, 1967, p 32.

(19) A. Immirzi, *Ric. Sci.*, **37**, 743, 846, 850 (1967).

(20) Please, note that the term "stability" is not used here in the strictly thermodynamic, correct, meaning.

(21) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **13**, 1996 (1974); L. E. Manzer, *ibid.*, **15**, 2354 (1976).

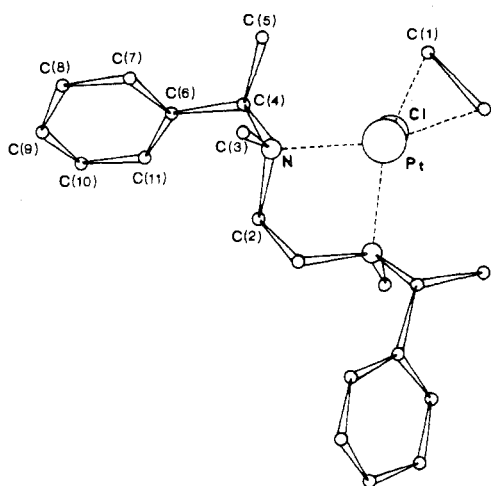


Figure 1. Perspective view of the molecular structure of $[\text{PtCl}_2(\text{C}_2\text{H}_4)(R,R\text{-mben})]$ showing geometry and atomic numbering.

Molecular Structure of $[\text{PtCl}_2(\text{C}_2\text{H}_4)(R,R\text{-mben})]$. The geometry of the inner coordination sphere of the platinum atom is trigonal bipyramidal, with the assumption that the ethene molecule is monodentate. The chlorine atoms occupy the axial positions, whereas the ethene and the nitrogen atoms of the diamine occupy the equatorial positions. A molecular model of complex **1** is shown in Figure 1, and bond lengths and bond angles are reported in Table V. The geometry around the platinum atom is in agreement with that found²² for an analogous five-coordinated platinum(II)-olefin complex. The axial Pt-Cl bond lengths do not differ from those reported²³ for a series of square-planar complexes, while the Pt-N distance shows that the equatorial covalent radius of five-coordinate platinum(II) is longer than that observed²⁴ in four-coordinated compounds. Moreover, the Pt-N bond length is also significantly longer than the Pt-N(sp²) value given²² for another five-coordinate platinum(II) complex. The Pt-C distance is substantially in the same range as those observed²⁵ in platinum(0)-olefin complexes. The C-C distances and the C-C-C angles in the benzene ring have mean values of $1.38 \pm 0.06 \text{ \AA}$ and $119.9 \pm 3^\circ$, respectively. The other geometrical parameters involving the light atoms appear acceptable only by taking into account the large standard deviations associated. In particular, the bond distance C(1)-C(1') is surprisingly large ($1.57(4) \text{ \AA}$) and is certainly beyond any reasonability. However, since the same trend is observed also for complex **2**, we believe that this may be indicative of a decrease of the bond order. The geometrical parameters of the amine groups indicate a distorted tetrahedral environment of the nitrogen atoms showing *R* configuration. No particularly short distances are present in the molecular packing.

The most interesting feature shown by the molecular structure appears to be the complete asymmetric induction observed on the two prochiral nitrogen atoms. This is also observed in the propene complex. In both cases the nitrogen atom configuration is *R,R*. This means that equal substituents on the nitrogen atoms are placed on opposite sites of the equatorial plane of the complex.

Molecular Structure of $[\text{PtCl}_2(\text{CH}_3\text{CH}=\text{CH}_2)(R,R\text{-mben})]$. The presence of the propene ligand in the place of ethene does

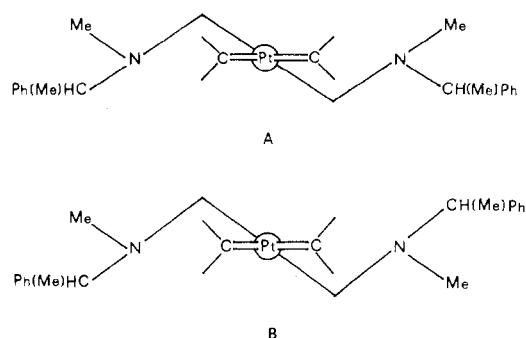


Figure 2. Schematic view of $[\text{PtCl}_2(\text{olefin})(R,R\text{-mben})]$ complexes along the equatorial plane showing the two coordinated nitrogen atoms in opposite (A) and equal (B) absolute configurations. The chlorine atoms are omitted for clarity.

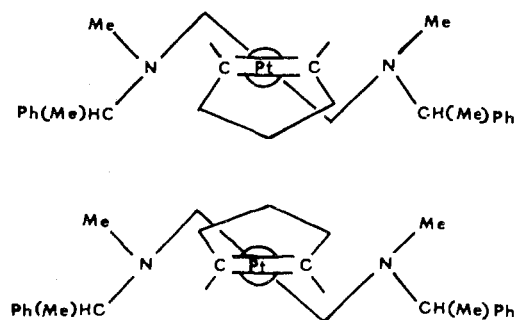


Figure 3. The two geometrical isomers arising in case the two coordinated nitrogen atoms of *R,R*-mben have opposite absolute configuration.

not cause substantial modifications on the molecular geometry, as observed in the former complex. In fact, the geometrical parameters (Table V) are quite similar to those reported for the ethene complex. In the benzene ring the C-C distances and the C-C-C angles have mean values of $1.40 \pm 0.03 \text{ \AA}$ and $120.0 \pm 3^\circ$, respectively. The values of the geometrical parameters of the propene group are greatly affected by the disorder of this ligand. This unfortunate situation makes it hard to correlate, as far as the olefinic prochiral ligand is concerned, the solid-state configuration to that shown by ¹H NMR data in solution (see below).

Nuclear Magnetic Resonance Studies. ¹H NMR spectroscopy is in principle a valuable tool to get information on four relevant features concerning the stereochemistry of $[\text{PtCl}_2(\text{olefin})(R,R\text{-mben})]$ complexes: (1) the relative configuration of the two coordinated nitrogen atoms of the *R,R*-mben ligand (Figure 2); (2) the rotation of the unsaturated ligand around the $\parallel\text{-Pt}$ axis; (3) the existence of a geometrical isomerism, in case the $\parallel\text{-Pt}$ axis is not a twofold axis (Figure 3); (4) the configuration of the prochiral =CHR groups of the unsaturated ligand after coordination.

Actually the number of resonances that can be observed for each set of protons, which are chemically equivalent in the free ligand, depends on more than one of the above-quoted factors. However, with the aid of the reported structural analyses, some unambiguous conclusions can be drawn. ¹H NMR spectra were recorded at 270 MHz for all the synthesized complexes, as well as for the already known² ethene and propene compounds.

The ¹H NMR spectrum of $[\text{PtCl}_2(\text{C}_2\text{H}_4)(R,R\text{-mben})]$ (**1**) shows diamine resonances whose multiplicity is unchanged with respect to the free ligand. The olefinic protons give rise to a unique AA'BB' multiplet²⁶ centered at δ 3.67 with ²J(¹⁹⁵Pt-H)

(22) L. Maresca, G. Natile, M. Calligaris, P. Delise, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 2386 (1976).

(23) Lj. Manojlovic-Muir and K. W. Muir, *Inorg. Chim. Acta*, **10**, 47 (1974).

(24) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960); E. Benedetti, C. Corradini, and C. Pedone, *J. Organomet. Chem.*, **18**, 203 (1969); C. Pedone and E. Benedetti, *ibid.*, **29**, 443 (1971).

(25) J. M. Baraban and J. A. McGinney, *J. Am. Chem. Soc.*, **97**, 4232 (1975).

(26) A singlet is observed at 60 MHz; see ref 2.

= 71 Hz. This pattern suggests that this complex has a twofold axis corresponding to the \parallel -Pt axis. This means that the two coordinated *R,R*-mben nitrogens must have the same absolute configuration, and, moreover, only one of the two possible stereoisomers, *N(R),N'(R)* or *N(S),N'(S)*, is present in solution. Should this not be the case the *N-CH₃* and *N-CH-CH₃* resonances would double as a consequence of the lack of any symmetry relationship correlating the halves of the coordinated diamine. This finding is in agreement with the results of the X-ray structural analysis, and it is quite reasonable to suppose that the absolute configurations of the nitrogen atoms in solution are identical with those, *N(R),N'(R)*, found in the solid state. At any rate the relative configuration of the nitrogen atoms appears to be markedly dependent on that of the adjacent carbons. Additional evidence is offered by the ¹H NMR spectra of complex **8**, where the asymmetric carbon atoms have opposite configurations. In fact, for **8**, as in the previous case, diamine resonances have unchanged multiplicity with respect to the free ligand. Moreover, the ethene protons at room temperature give rise to a broad signal which sharpens above 40 °C. These features can only be interpreted as due to the nitrogens having opposite configuration. Otherwise, the lack of symmetry would afford two sets of signals for *N-CH₃* and *N-CH-CH₃* protons. The quoted findings also point out that in complex **8** the rotation of the ethene ligand around the \parallel -Pt axis is hindered at room temperature. No information can be obtained on this point for complex **1**, because of the presence of the twofold axis.

The ¹H NMR spectra of complexes **2**, **3**, and **4** containing monosubstituted olefins (propene, AA, AN) are complicated by all of the four quoted factors. However, the experimental data have shown that, in spite of the remarkable differences in the ¹H NMR spectra, these three complexes can be similarly described from a stereochemical point of view. In particular the spectrum of complex **3** shows that only one stereoisomer is present in solution: in fact, two equally intense sets of signals for each set of *R,R*-mben protons and a single ABX pattern for the olefinic protons of AA are observed. Two stereoisomers in the approximate ratio 1:4 are present in solution for complex **2**: for each isomer a spectral pattern similar to the one of complex **3** is observed.²⁷ Finally, two stereoisomers in time-dependent ratios with ¹H NMR spectral patterns similar to those of complexes **2** and **3** are found in solution for complex **4**.

A reliable interpretation of these experimental data leads us to ascribe, in all three complexes, the same absolute configuration to the coordinated nitrogens of *R,R*-mben, probably the same observed in the ethene complex. We wish to point out that the complexes are obtained by olefin exchange from the ethene complex in mild conditions. Moreover, the attributed configuration is the one presented in solid state by the propene complex. On the basis of the above assignment, a hindered rotation of the olefin in complexes **2**, **3**, and **4** is inferred by the nonequivalence of the corresponding protons of the halves of the coordinated *R,R*-mben. The coalescence of the two sets of the diamine signals into a single set, which is obtained above 40 °C, gives evidence that the olefin rotation is hindered at room temperature, while independently supporting the attribution of equal configurations to the diamine nitrogen atoms.

On these grounds, the coordination of prochiral AA has to be quite stereoselective, while a moderate inductive effect is inferred for the propene complex (in the above quoted 1:4 ratio). In the case of the latter compound, the quoted ratio is time independent in solution. However, no correlation be-

tween the chirality of the olefin in solution and the one in solid state can be made since the X-ray structural analysis of the complex does not allow any configurational assignment of the coordinated propene ligand (vide supra). The coordination of AN is also affected by the presence of the other centers of asymmetry. The absolute configuration of AN in the crystal phase which has been isolated appears to be opposite to the one observed in aged solutions. In fact, the ¹H NMR spectrum of freshly dissolved complex (about 2 min after dissolution) shows the presence of two stereoisomers in the approximate ratio 2:1 (as in the case of the propene complex). The ratio of the two stereoisomers changes with time, and an inversion of their relative abundances is observed (2:3 after 1 h).

The ¹H NMR spectrum of complex **5** shows a very simple pattern: diamine signals whose multiplicity is unchanged with respect to the free ligand and a single A₂ resonance for FN protons. This pattern is consistent with the presence in solution of a unique stereoisomer, in which the two nitrogens of *R,R*-mben have an equal configuration and only one of the two enantiotopic faces of FN is coordinated to platinum(II). Also in this case, as for the ethene complex, the \parallel -Pt axis is a twofold axis, which hinders the acquisition of information about the rotation of the unsaturated ligand. To overcome this difficulty, we attempted to synthesize [PtBrCl(FN)(*R,R*-mben)], which was obtained in mixture with the corresponding dibromo and dichloro complexes. A comparison between the ¹H NMR spectra of this mixture and of the two latter pure compounds allowed us to ascertain that, in the complex containing two different halogen atoms, the olefinic protons gave rise to an AB quartet. This result points out a hindered rotation of the FN ligand.

In the case of complexes **6** and **7** containing an unsaturated ligand of C_{2v} symmetry (MA and MI), the ¹H NMR spectra (unaffected up to 70 °C) show two equally intense sets of signals for each set of *R,R*-mben protons and a single AB quartet for the olefinic protons. In these cases the spectra are consistent with the presence in solution of a single stereoisomer in which the two nitrogen atoms of *R,R*-mben still have the same absolute configuration, while the rotation of the unsaturated ligand is hindered. For these complexes an alternative hypothesis could be proposed with the assumption of the nitrogen atoms of *R,R*-mben in opposite configuration and the unsaturated ligand in only one geometrical position with respect to the equatorial plane of the complex (Figure 3). However, we wish to emphasize that the complexes are obtained by olefin exchange from the corresponding ethene complex, and we have no experimental evidence whatsoever that this procedure has caused some change in the configuration of the nitrogen atoms of *R,R*-mben in any of the previously examined complexes.

Conclusions

The solid-state data as well as the behavior in solution have shown that the asymmetric carbon atoms of *R,R*-mben are responsible for a complete asymmetric induction effect on the configuration of the coordinated nitrogens in the [PtCl₂(olefin)(*R,R*-mben)] complexes. Within the examined cases, this effect is independent of the nature of the unsaturated ligand.

In addition, we have found that in at least two cases the coordination of a prochiral olefin is completely stereoselective.

Finally, we have obtained some preliminary results concerning the rotation of the unsaturated ligand around the \parallel -Pt axis, indicating that the activation free energy is higher²⁸ than that found for platinum(II) square-planar complexes.

Acknowledgment. The authors appreciate the helpful discussions with Professor A. Panunzi. This research was sup-

(27) This pattern is clearly observed at temperatures below 20 °C. At higher temperature, the *N-CH₃* and *N-CH-CH₃* signals appear as broad unsymmetrical singlets.

(28) L. Paolillo, private communication.

ported by the Italian National Research Council (CNR).

Registry No. 1, 66945-55-9; 2 (isomer 1), 72656-95-2; 2 (isomer 2), 72656-96-3; 3, 72581-96-5; 4 (isomer 1), 72581-97-6; 4 (isomer 2), 72598-31-3; 5, 71930-15-9; 6, 72581-98-7; 7, 72581-99-8; 8, 72598-32-4; 9, 71930-13-7; 10, 72582-00-4; PtBrCl(C₂H₄)(R,R-mben), 71930-14-8; PtBrCl(FN)(R,R-mben), 72582-01-5; potassium tri-

chloro(ethene)platinate(1-), 12012-50-9; potassium tribromo(ethene)platinate(1-), 12175-83-6.

Supplementary Material Available: Listings of observed and calculated structure factors for [PtCl₂(C₂H₄)(R,R-mben)] and [PtCl₂(CH₃CH=CH₂)(R,R-mben)] (8 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois, the Chemistry Department, Nuclear Research Centre Negev, Beer-Sheva, Israel, and the Institut für Anorganische Chemie, Technische Universität Hannover, Hannover, Federal Republic Germany

Activation Energies for an Intramolecular Electron Transfer Reaction¹

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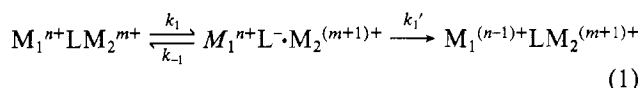
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Activation energies and solvent effects for the intramolecular electron transfer reaction from a ligated *p*-nitrobenzoate radical anion to a cobalt(III) center in the complexes formed by the reduction of I and II were measured. The rate of the intramolecular electron transfer reaction decreases with increasing solvent polarity. The activation energies range between 9.0 and 12.5 kcal/mol for complex I and between 13.3 and 19.5 kcal/mol for complex II. The rates always followed Arrhenius temperature dependence, even with 10⁴ changes in rate from room temperature to 203 K. Very large preexponential factors, 2 × 10¹¹–10¹⁸ s⁻¹, are calculated for these rate constants.

Introduction

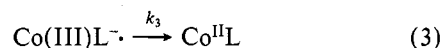
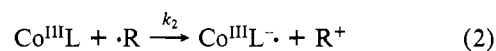
Recently several groups have reported the kinetics of intramolecular electron transfer, ET, reactions in complexes of the type M₁LM₂³⁻¹³ (where M₁ and M₂ represent the oxidizing and reducing metal cations with their ligand spheres and L is the bridging ligand). The study of such ET reactions is of importance as it represents one of the elementary steps in inner sphere intramolecular ET reactions^{14,15} and as it presents an opportunity to study the factors affecting ET through ligands of different chemical nature.

In some cases the ET reaction in M₁LM₂ is directly from M₁ to M₂ without a "coupling mechanism" through the ligand.^{4,7} In these cases the ET reaction can be viewed as proceeding via an outer sphere mechanism. The ligand L serves mainly to keep the two reacting centers in close proximity. However in most systems studied orbital coupling through the bond systems of the ligands supplies the route for the ET process. In many of these cases the ET can be described as a two-step process: reduction of L by M₂ followed by the reduction of M₁ by the anion radical L⁻. This is known as the "chemical mechanism".¹⁵



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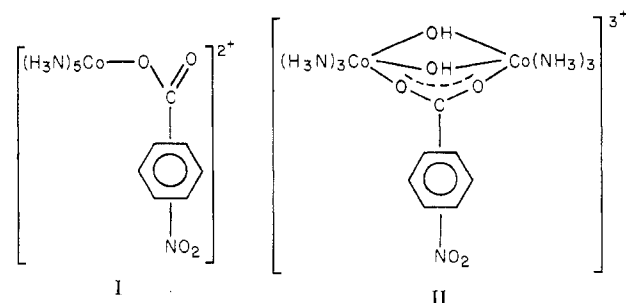
Evidently the measurement of the kinetics of ET in the latter case supplies information on a relatively complex system. It is therefore of interest that recent studies have shown that it is possible to reduce Co^{III}L, where L ≡ *p*-nitrobenzoate^{16,17} or pyrazinecarboxylate¹⁸ bound to the cobalt through the carboxylate, by free radicals, e.g., e_{aq}⁻, CO₂⁻, (CH₃)₂COH via the mechanism



and that *k*₃ can thus be directly measured.

This and predictions, by modern radiationless transition theories of electron transfer, of non-Arrhenius behavior^{19,20} stirred us to study reaction 3 over a wide temperature range. A hoped for result of decreased or even zero activation energies at low temperature, less than 150 K, was not found. The reactions we studied remained strongly activated and became too slow for our measurement techniques at about 200 K.

The compounds chosen for this study (I and II) were pre-



viously shown to be reduced by (CH₃)₂COH radicals via reactions 2 and 3.^{16,17} The rate of reaction 3 was found to be

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