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Five-Coordinate [Pt^{II}Cl$_2$(η^2-olefin)L$_2$] (L$_2$ = σ,σN,N'-Bonded α-Diimine or N,N'-Disubstituted 1,2-Diaminoethane) Complexes. Solution Conformation, η^2-Olefin Rotational Barriers (NMR), and the X-ray Molecular Structure of [PtCl$_2$(η^2-styrene)(*t*-Bu-N=CHCH=N-*t*-Bu)][1]

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Five-coordinate platinum–olefin complexes [PtX$_2$(η^2-olefin)L$_2$], in which L$_2$ is the bidentate ligand RN=CHCR'=NR (α-diimine) or RN(H)CH$_2$CH$_2$N(H)R (N,N'-disubstituted 1,2-diaminoethane), were synthesized in almost quantitative yield by reaction of K[PtCl$_3$(η^2-olefin)] with the L$_2$ ligand. The solid-state structure of [PtCl$_2$(η^2-styrene)(*t*-BuNCHCHN-*t*-Bu)], a representative of this class of compounds, was established by X-ray diffraction analysis. In the trigonal-bipyramidal structure, the diimine ligand and the olefin occupy the equatorial plane with the Cl atoms in the axial sites. The phenyl ring of the η^2-bonded styrene is bent back from C=C skeleton (C—C = 1.53 (5) Å) by 27°. Extensive ^{1}H and ^{13}C NMR measurements confirmed that the five-coordinate structure found in the solid (IR, Raman, and ^{35,37}Cl NQR spectroscopic data) is retained in solution. Study of the solution dynamic behavior of the [PtX$_2$(η^2-olefin)L$_2$] compounds revealed that (i) the Pt–N interaction of the σ,σN,N'-bonded L$_2$ ligand is inert on the NMR (^{15}N and ^{195}Pt) time scale, (ii) no platinum–olefin bond dissociation occurs in the range –60 to +34 °C (concluded from ^{13}C and ^{1}H NMR data for compounds containing both a prochiral R group (e.g. CMe$_2$Et) in L$_2$ and a prochiral olefin (e.g., styrene)), (iii) the ligand L$_2$ does not take part in stereoisomerization processes, and (iv) pure rotation of the olefin around the platinum–olefin bond axis can fully account for the observed temperature dependence of the NMR spectra. The barrier to olefin rotation in these five-coordinate platinum compounds studied ranges from 13.2 (styrene) to 15.9 (methylacrylate) kcal/mol. Our data suggest (i) in [PtCl$_2$(η^2-olefin)L$_2$] the barrier to rotation is determined by steric factors, i.e., by the axial halide ligands which are cis to the olefin (cf. square-planar *trans*-[PtCl$_2$(η^2-olefin)L]) and (ii) the equatorial diimine ligand by virtue of its flat conformation represents a ligand with a minimal steric influence on the axial ligands. As a result of rapid N–H bond dissociation/association processes (established by H/D exchange experiments), [PtCl$_2$(η^2-styrene)(EtMe$_2$C-diam)] does not exist in solution as a mixture of the expected diastereomers.

Introduction

Recently we reported the synthesis and characterization of Pd^{II}, Pt^{II} and Rh^I complexes containing α-diimine ligands. The R-dim[2] ligand in these complexes is either σN,σN' bridging,[3–5] σN monodentate,[3,6] or σN $\rightleftharpoons$ σN' fluxional[5] bonded to the metal. Extensive NMR studies of the Pd (^{1}H, ^{13}C, ^{31}P) and Pt (^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{195}Pt) complexes with a σN $\rightleftharpoons$ σN' bonded R-dim ligand, e.g., [PtCl$_2$(PBu$_3$)(*t*-Bu-dim)], revealed that the fluxional process involved a five-coordinate transition state or intermediate as is shown in Figure 1.[6,7] The five-coordinate configuration B is very similar to the configuration of the intermediates proposed in the fluxional process of cationic [PtCl(PEt$_3$)$_2$(NN)]$^+$ (NN = phen or bpy) species.[8] Unlike the phen and bpy ligands, it is to be noted that the R-dim ligand in the anti conformation can function in a monodentate manner, resulting in configurations A or A' which were found to be stable on the NMR time scale at low temperature.[6] In the case of the R-dim–Pd complexes, these σN monodentate-bonded forms become further stablized when instead of a trans phosphine ligand a second R-dim ligand is present; e.g., *trans*-[PdCl$_2$(R-dim)$_2$] has a temperature-independent ^{1}H NMR spectrum.[3,6]

Interestingly, stabilization of a five-coordinate transition state or intermediate (B) of [PtCl$_2$(PBu$_3$)(R-dim)] was made possible by substitution of the phosphine for an olefinic ligand.

In this paper we report the synthesis and characterization of various types of five-coordinate Pt–olefin complexes [PtX$_2$(η^2-olefin)(R-dim)] and [PtCl$_2$(η^2-olefin)(R-diam)]. Recently, [PtCl$_2$(η^2-C$_2$H$_4$)L$_2$] complexes[9,10] in which L$_2$ was a bidentate N-donor ligand were independently reported. The structure of [PtCl$_2$(η^2-styrene)(*t*-Bu-dim)], which was elucidated by X-ray analysis and which confirmed the five-coordinate geometry of the central Pt^{II} atom, has been the subject of a preliminary communication.[4] These five-coordinate α-diimine complexes were found to be excellent starting materials for the preparation of the related R-diam complexes [PtCl$_2$(η^2-C$_2$H$_4$)(R-diam)] by direct ligand substitution.[11]

The bidentate and olefinic ligands in these complexes were selected such that a study of the expected rotation of the olefin around the Pt–olefin axis would be feasible by ^{1}H and ^{13}C NMR spectrometry. The resultant data are compared with those established for five-coordinate [Fe(CO)$_4$(η^2-olefin)], square-planar [Pt^{II}Cl(η^2-olefin)LL'] (LL' = monoanion) and trigonal-planar [Pt^0(η^2-C$_2$H$_4$)$_{3-n}$(PR$_3$)$_n$] (n = 1, 2) complexes. Such information is timely in view of the theoretical analysis of olefin–ML$_n$ rotational barriers reported recently by Hoffmann et al.[12] and Ziegler and Rauk.[13]

Experimental Section

Preparation of the Compounds. α-Diimines (R-dim =

(1) *a,e*-Dichloro-*b*-(η^2-styrene)-*c,d*-(σ,σN,N'-2,2,7,7-tetramethyl-3,6-diaza-3,5-octadiene)platinum(II).

(2) Throughout this paper the α-diimines (RNCHCHNR) are abbreviated as R-dim and the N,N'-disubstituted 1,2-diaminoethanes (RN(H)-CH$_2$CH$_2$N(H)R) as R-diam.

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Table I. Analytical Data of [PtX₂(η²-olefin)(R-dim)] and [PtCl₂(η²-olefin)(R-diam)]

	% C		% H		% N		% Cl or Br		mol wt^a		T_i,^{b} °C	T_f,^{c} °C	ΔH_r,^{d}
	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd			
[PtCl₂(η²-C₂H₄)(*i*-Pr-dim)]	28.07	27.66	4.72	4.64	6.52	6.45	15.55	16.33			103	144	−1.0 ± 0.1
[PtCl₂(η²-C₂H₄)(*t*-Bu-dim)]	31.14	31.18	5.20	5.23	6.15	6.06	15.22	15.34	476.2	462.3	105	171	−7.2 ± 0.2
[PtBr₂(η²-C₂H₄)(*t*-Bu-dim)]	26.46	26.15	4.35	4.39	5.16	5.08	28.99	28.99	538.1	551.2	125	208	
[PtCl₂(η²-C₂H₄)(EtMe₂C-dim)]	34.32	34.29	5.78	5.76	5.69	5.71	14.34	14.46	497.7	490.4	100	139	−7.1 ± 0.4
[PtCl₂(η²-C₂H₄)(*i*-Pr-NCCH₃CHN-*i*-Pr)]	29.57	29.47	4.95	4.52	6.28	6.25	15.59	15.81					
[PtCl₂(η²-C₂H₄)(*t*-Bu-diam)]	30.91	30.90	5.95	6.05	6.05	6.01	15.19	15.20	473.0	466.4	51	158	
[PtCl₂(η²-*cis*-CH₃C₂H₂CH₃)(*t*-Bu-dim)]	34.40	34.29	5.74	5.75	5.78	5.71	14.74	14.46			80	166	
[PtCl₂(η²-*cis*-CH₃C₂H₂CH₃)(EtMe₂C-dim)]	37.23	37.06	5.94	6.22	5.30	5.40	13.87	13.67					
[PtCl₂(η²-C₂H₃C₆H₅)(*t*-Bu-dim)]	39.51	40.15	5.33	5.24	5.13	5.20			499.4	538.4	55	147	
[PtBr₂(η²-C₂H₃C₆H₅)(*t*-Bu-dim)]	34.64	34.46	4.52	4.50	4.46	4.46	25.49	25.48	609.7	627.3	112	136	
[PtCl₂(η²-C₂H₃C₆H₅)(EtMe₂C-dim)]	42.29	42.40	5.67	5.69	4.96	4.95	12.43	12.51	511.5	566.5	50	130	
[PtCl₂(η²-C₂H₃C₆H₅)(EtMe₂C-diam)]	42.26	42.25	6.41	6.03	4.95	4.93	12.60	12.47			72	120	

^{a} In chloroform; 34 °C. ^{b} Initial temperature. ^{c} Final temperature for decomposition. ^{d} Reaction enthalpy.
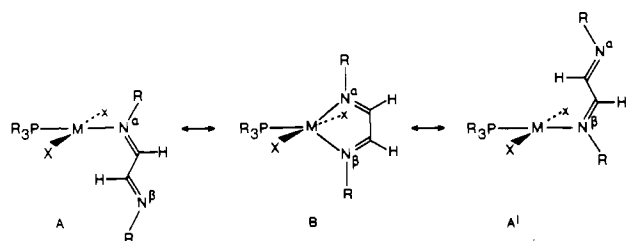

Figure 1. Proposed mechanism for the fluxional behavior of the [MCl₂(PR₃)(R-dim)] complexes in solution.[6]

Scheme I

RNCR'CHNR, R' = CH₃, H) and N,N'-substituted 1,2-diamino-ethanes (R-diam = RN(H)CH₂CH₂N(H)R) were prepared by methods described elsewhere.[14] The starting complexes K[PtX₃(η²-olefin)] (X = Cl, Br; olefin = ethylene, *cis*-, and *trans*-2-butene) were prepared by the method of Orchin et al.[15] K[PtCl₃(η²-styrene)] was obtained in high yield from the stirred reaction mixture of K-[PtCl₃(η²-C₂H₄)] in methanol with excess styrene (1/5 molar ratio) for 24 h.

The preparations of the new metal complexes, carried out in a N₂ atmosphere, are described below. Solvents were dried and distilled before use.

[PtX₂(η²-olefin)(R-dim)] and [PtX₂(η²-olefin)(R'-diam)] (X = Cl, Br; olefin = ethylene, *cis*- and *trans*-2-butene, styrene; R = *i*-Pr, *t*-Bu, EtMe₂C; R' = *t*-Bu, EtMe₂C). R-dim (or R-diam) (1.2 mmol) was added to a stirred solution of K[PtX₃(η²-olefin)] (1 mmol) in acetone (10 mL), and after 5 min the solution was filtered (removal of KX). The filtrate was evaporated and yellow microcrystalline [PtX₂(η²-olefin)(R-dim)] (or [PtX₂(η²-olefin)(R-diam)]) was obtained by addition of methanol (10 mL) (olefin = ethylene) or hexane (10 mL) (olefin = 2-butene, styrene). The crystals were collected by filtration, washed with hexane (5 × 15 mL) (removal of R-dim or R-diam), and dried in vacuo at room temperature; yield 70–80%. If necessary, further purification could be achieved by recrystallization from a dichloromethane–hexane mixture. Molecular weight, analytical, and physical data are given in Table I.

Physical Measurements. Microanalyses were performed under the supervision of Mr. W. J. Buis of the Institute for Organic Chemistry TNO, Utrecht, the Netherlands. Molecular weights were measured in chloroform with use of a 302B Hewlett-Packard vapor pressure osmometer.

¹H NMR spectra were recorded on a Varian T-60 or HA-100 spectrometer with tetramethylsilane (Me₄Si) as internal standard; ¹³C NMR spectra were obtained on a Varian CFT-20 using Me₄Si as internal standard. NQR spectra were obtained with a Wilks NQR 1A spectrometer.

Infrared spectra were measured on a Beckman 4250 spectrophotometer as Nujol mulls between CsI plates or as KBr pellets. Raman spectra were obtained on a Ramanor HG 25 Raman spectrophotometer
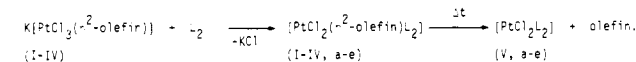
with the use of a spinning cell[16] because of the photosensitivity of the compounds.

Thermographic measurements were carried out in a N₂ atmosphere on a Mettler TA1 thermobalance. A Du Pont 990 differential scanning calorimeter was used for the caloric measurements.

Calculations of the ΔG*'s for the Olefin Rotation. Values for the free energy of activation were calculated by using the expression $\Delta G^*_{T_c} = -RT \ln \pi \Delta \nu h / 2^{1/2} kT$ where $\Delta \nu$ represents the chemical shift difference ($\Delta \delta$ in Hz) of the coalescing peaks in the absence of exchange, T represents the coalescence temperature, and R, k, and h have their normal thermodynamic significances.[17]

X-ray Structure Determination of [PtCl₂(η²-styrene)(*t*-Bu-dim)]. Yellow crystals of [PtCl₂(η²-styrene)(*t*-Bu-dim)] were obtained from a dichloromethane–hexane solution. They are monoclinic, space group *Cn* with four molecules in a unit cell of dimensions a = 12.2146 (5) Å, b = 15.5558 (8) Å, c = 12.3919 (5) Å, and β = 119.38 (1)°; d_{calcd} = 1.74 g cm⁻³. A total number of 1174 reflections with intensities above the 2.5σ level were collected on a Nonius CAD-4 diffractometer using graphite-monochromatized Cu Kα radiation. No absorption correction was applied: crystal dimension 0.4 × 0.1 × 0.1 mm, μ = 153.9 cm⁻¹. The positions of the Pt and Cl atoms were derived from an (E^2 − 1)-Patterson synthesis. The remaining nonhydrogen atoms were located in a subsequent difference Fourier synthesis. Refinement was carried out by means of anisotropic block-diagonal least-squares calculations. The H atoms were introduced at their calculated positions and not refined. A weighting scheme $w = (7.1 ± F_o + 0.012F_o^2)^{-1}$ was applied. The final R was 0.048.

Results

Synthesis of [PtX₂(η²-olefin)(R-dim)] and [PtCl₂(η²-olefin)(R-diam)]. Complexes of the type [PtX₂(η²-olefin)(R-dim)] and [PtX₂(η²-olefin)(R-diam)] (I–IV) have been isolated in almost quantitative yield from the 1/1 molar reactions of K[PtX₃(η²-olefin)] with the respective R-dim or R-diam ligand. An alternative synthetic route which also led to isolation of pure R-diam complexes involved substitution of the ligand L from [PtX₂(η²-C₂H₄)L] complexes (L is monodentate pyridine derivative or R-dim).[11]

The stoichiometry of the complexes (I–IV) was established by elemental analysis (see Scheme I and Table I). Molecular weight determinations by osmometry (34 °C) established that I–IV exist as monomers in chloroform (see Table I). They are nonelectrolytes in acetone.

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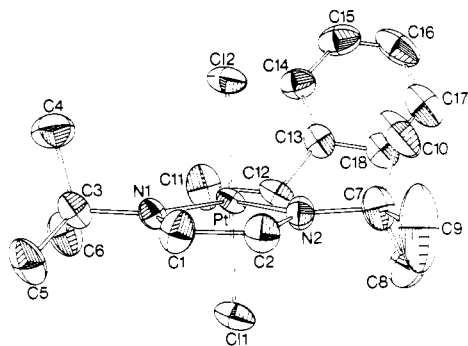
Figure 2. ORTEP drawing showing the molecular structure of [PtCl$_2$(η^2-styrene)(t-Bu-dim)] (vibrational ellipsoids scaled to include 40% probability).

Table II. Relevant Bond Distances (Å) and Interbond Angles (Deg) with Estimated Standard Deviations in Parentheses

Pt–Cl(1)	2.299 (9)	Cl(1)–Pt–Cl(2)	179.8 (3)
Pt–Cl(2)	2.323 (8)	Cl(1)–Pt–N(1)	89.3 (7)
Pt–N(1)	2.20 (3)	Cl(1)–Pt–N(2)	88.5 (7)
Pt–N(2)	2.31 (3)	Cl(1)–Pt–C(11)	92.1 (10)
Pt–C(11)	2.16 (4)	Cl(1)–Pt–C(12)	87.8 (10)
Pt–C(12)	2.20 (4)	Cl(2)–Pt–N(1)	90.7 (7)
N(1)–C(1)	1.28 (4)	Cl(2)–Pt–N(2)	91.6 (7)
N(1)–C(3)	1.46 (4)	Cl(2)–Pt–C(11)	87.8 (10)
N(2)–C(2)	1.28 (5)	Cl(2)–Pt–C(12)	92.1 (10)
N(2)–C(7)	1.44 (5)	N(1)–Pt–N(2)	74.7 (10)
C(1)–C(2)	1.51 (5)	N(1)–Pt–C(11)	123.4 (12)
C(11)–C(12)	1.53 (5)	N(1)–Pt–C(12)	164.1 (12)
C(14)–C(13)	1.47 (6)	N(2)–Pt–C(11)	161.9 (12)
		N(2)–Pt–C(12)	120.8 (11)
		C(11)–Pt–C(12)	41.2 (12)
		C(11)–C(12)–C(13)	123.0 (3)

Structure of [PtX$_2$(η^2-olefin)(L$_2$)] Species in the Solid. The X-ray Structure of [PtCl$_2$(η^2-styrene)(t-Bu-dim)]. The solid-state molecular structure of [PtCl$_2$(η^2-styrene)(t-Bu-dim)] was determined not only to establish the five-coordinate nature and ligand geometry of the [PtX$_2$(η^2-olefin)L$_2$] complexes but also to study the degree of distortion of the olefin skeleton in such species. The crystal structure consists of discrete monomeric [PtCl$_2$(η^2-styrene)(t-Bu-dim)] units (see Figure 2). Relevant bond angles and distances are presented in Table II. The platinum atom is in the center of a trigonal-bipyramidal array. The C=C bond of the styrene molecule and the CN=CC=NC skeleton of the σ,σN,N'-bonded t-Bu-dim ligand reside in the equatorial plane (plane 1 deviations for the best plane through Pt, N(1, 2), and C(1, 2, 11, 12): Pt, –0.02; N(1), 0.04; N(2), –0.03; C(11), –0.05; C(12), 0.06; C(1), 0.21; C(2), 0.21 Å). The Cl atoms occupy axial positions with a linear lineup of the Cl and Pt atoms (Cl–Pt–Cl 179.8 (3)°).

The geometry around the platinum atom is identical with that observed for a recently reported five-coordinate platinum–olefin complex [PtCl$_2$(η^2-propene)(R,R)-N,N'-dimethyl-N,N'-bis(α-methylbenzyl)-1,2-ethanediamine].[18] The diimine ligand displays a characteristic bite angle of 74.7 (10)°,[5] resulting in a considerable distortion of the angles in the equatorial plane from the ideal trigonal bipyramid. Comparison of the structures of Pt–propene and Pt–styrene complexes which differ in the type of L$_2$ ligand show that these structures contain similar Pt–Cl and Pt–C(olefin) distances. The Pt–N distances in the R-dim complex are slightly longer than the mean Pt–N distance found in the four-coordinate [(PtCl$_2$(PBu$_3$))$_2$(t-Bu-dim)] complex. In the latter complex, the t-Bu-dim ligand is bridging between two $trans$-Cl$_2$Pt(PBu$_3$) centers (Pt–N = 2.214 (10 Å).[5]

An interesting aspect of the present structure is the fact that the C̅=̅C̅ part of the styrene molecule is coplanar with the P̅t̅–̅N̅C̅C̅N̅ plane. In the four-coordinate styrene–Pt complexes [PtCl$_2$(η^2-styrene-R)(NC$_5$H$_4$X)], reported by Nyburg et al.,[19] the C=C unit is slightly twisted out of the upright conformation (80° with respect to the coordination plane). Furthermore, the C=C unit is coplanar with phenyl ring in the five-coordinate styrene platinum complex (plane 2 deviations from the best plane through C(11)–C(18): C(11), –0.03; C(12), 0.00; C(13), 0.05; C(14), 0.02; C(15), –0.01; C(16), –0.01; C(17), –0.01; C(18), 0.00 Å).

In contrast with the failure to locate the CH$_3$ group of propene in [PtCl$_2$(η^2-propene)((R,R)-N,N'-bis(α-methylbenzyl)-1,2-ethanediamine)],[18] the position of the phenyl ring carbon atoms could be unambiguously resolved. This allowed the determination of the extent of bending back of the phenyl group from the plane perpendicular to plane 1 and containing the C=C atoms. Defining this angle according to Nyburg et al., we find angle of 27° being the supplements of the angles between planes 1 and 2. This value is slightly larger than the angles (16.5–18.5°) found in the four-coordinate [PtCl$_2$(η^2-styrene-R)(NC$_5$H$_4$X)] complexes.[19]

IR, Raman, and ^{35,37}Cl NQR Spectroscopy. The IR and Raman spectroscopic data (Table III) from [PtCl$_2$(η^2-styrene)(t-Bu-dim)] and the other [PtX$_2$(η^2-olefin)L$_2$] (L$_2$ = R-dim or R-diam) complexes pointed to a similar trigonal-bipyrimidal coordination geometry for all these complexes in the solid state. Assignment of ν(C=N) was made for the compounds I–III and V with the data showing an increase of about 30 cm^{-1} on going from a four-coordinate ([PtCl$_2$(R-dim)]) to the five-coordinate structure (cf. ref 7). The presence of electron-releasing groups on the C=C unit, which is coplanar to the R-dim skeleton, results in a further increase (cf. [PtCl$_2$(η^2-olefin)(t-Bu-dim)]: ethylene 1590 cm^{-1} vs. cis-2-butene 1610 cm^{-1}). It seems plausible that increased electron density on the platinum from the olefin is compensated for by a decrease of the σ donation from the diimine ligand, the resulting increase in electron density in the C=N bond then being reflected in the larger ν(C=N) value. The influence of the halogen atoms on ν(C=N) is small, cf. the similar values for the Cl (1590 cm^{-1}) and Br (1584 cm^{-1}) derivatives of [PtX$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)].

Unique to the [PtCl$_2$(η^2-olefin)(R-diam)] complexes is the observation in both IR and Raman spectra of the characteristic N–H stretching mode (see Table III).

The equivalence of the halogen atoms in the [PtCl$_2$-(η^2C$_2$H$_4$)(R-dim)] (R = i-Pr, t-Bu) was demonstrated by the observation of only one resonance pattern in ^{35,37}Cl NQR spectra. The two signals at 22.280 and 17.685 MHz (R = i-Pr-dim) are assigned to ^{35}Cl and ^{37}Cl, respectively. These are increased by 0.8–1.9 MHz with respect to values for ^{35}Cl and ^{37}Cl in square-planar $trans$-[PtCl$_2$(η^2-olefin)L] (L = pyridine derivatives).[20] In these latter complexes, the charge on chlorine ρ-^{35}Cl, calculated on the basis of the elementary Townes–Daily consideration,[21] is 0.611–0.628 whereas for our five-coordinate species one obtains a value of 0.594, indicating a small relative increase in the Pt–Cl bond covalency.

Thermogravimetric Analysis. The thermal stability of solid [PtX$_2$(η^2-olefin)(R-dim)] and [PtCl$_2$(η^2-olefin)(R-diam)] complexes was studied in some detail by TGA (thermogravimetric analysis measurements (see Table I). Distinct

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Table III. Infrared[a] and Raman[b] Spectra of [PtCl$_2$(R-dim)], [PrX$_2$(η^2-olefin)(R-dim)], and [PtCl$_2$(η^2-olefin)(R-diam)] Complexes

	ν(N-H), cm^{-1}	ν(C=N), cm^{-1}	ν_{as}(Pt-Cl), cm^{-1}	ν_s(Pt-Cl), cm^{-1}
[PtCl$_2$(i-Pr-dim)]		1566	336	322
[PtCl$_2$(t-Bu-dim)]		1560		326
[PtCl$_2$(EtMe$_2$C-dim)]		1571	336	320
[PtCl$_2$(η^2-C$_2$H$_4$)(i-Pr-dim)]		1596 (1592)	334	(338)
[PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)]		1590 (1595)	332	(330)
[PtBr$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)]		1584	256^c	
[PtCl$_2$(η^2-C$_2$H$_4$)(EtMe$_2$C-dim)]		1607 (1608)	332	(334)
[PtCl$_2$(η^2-C$_2$H$_4$)(i-PrNCCH$_3$-CHN-i-Pr)]		1600	332	
[PtCl$_2$(η^2-cis-CH$_3$C$_2$H$_2$CH$_3$)(i-Pr-dim)]		1611	340	
[PtCl$_2$(η^2-cis-CH$_3$C$_2$H$_2$CH$_3$)(t-Bu-dim)]		1610	340	
[PtCl$_2$(η^2-cis-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]		1605	334	
[PtCl$_2$(η^2-trans-CH$_3$C$_2$H$_2$CH$_3$)(t-Bu-dim)]		1611	333	310 (314)
[PtCl$_2$(η^2-trans-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]		1604	331	314
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(i-Pr-dim)]		1603	330	
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(t-Bu-dim)]		1603	332	
[PtBr$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(t-Bu-dim)]		1600	242^c	
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(EtMe$_2$C-dim)]		1598	335	
[PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-diam)]	3228 (3233) 3244^d 2385^e		336	(334)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(EtMe$_2$C-diam)]	3224		325	

^{a} As Nujol mulls. ^{b} As pure complex in parentheses. ^{c} ν(Pt-Br). ^{d} In chloroform. ^{e} In D$_2$O-saturated chloroform solution.

melting points were not observed, but it appeared that decomposition occurred in two specific steps: first, quantitative release of the olefin (detected by GLC) resulting in formation of cis-[PtX$_2$(R-dim)] and cis-[PtCl$_2$(R-diam)], respectively, which were identified by ^{1}H NMR in Me$_2$SO-d_6) and IR spectroscopy;[6] second, the decomposition of these four-coordinate complexes into PtX$_2$ and the free R-dim or R-diam ligands which were detected by GLC analyses.

Stereochemistry in Solution of [PtX$_2$(η^2-olefin)L$_2$]. Unlike the complexes [PtX$_2$(η^2-olefin)L$_2$] reported previously,[9] it should be noted that the complexes described in this paper have sufficient solubility and stability to allow an extensive study of their structure in solution by ^{1}H, ^{13}C, ^{15}N, and ^{195}Pt NMR spectroscopy.

The ^{1}H and ^{13}C NMR data of the free ligands L$_2$ and of the [PtX$_2$(η^2-olefin)L$_2$] complexes, which are monomeric and nonelectrolytes in CHCl$_3$, are given in Tables IV and V; two representative NMR spectra are given in Figure 3. The various aspects of the [PtX$_2$(η^2-olefin)(R-dim)] and [PtCl$_2$-(η^2-olefin)(R-diam)] complexes are described separately below.

(a) [PtX$_2$(η^2-olefin)(R-dim)]. The NMR data show that the proton resonances of the diimine ligand undergo a considerable downfield shift upon coordination in contrast to a small downfield shift of the ^{13}C resonances. The ^{1}H and ^{13}C resonance patterns of the complexes are consistent with retention in solution of a five-coordinate structure as found for [PtCl$_2$(η^2-styrene)(t-Bu-dim)] in the solid. This five-coordination was concluded from the following observations.

Isochronous resonances were found for the hydrogen and carbon atoms in the imino substituents, as well as singlet resonances for both the imine proton and imine carbon (N=C—H) at room temperature. These resonances were in several cases flanked by ^{195}Pt satellites. In particular, in the ^{13}C NMR spectra, ^{195}Pt couplings were observed for most if not all carbon resonances of the R-dim ligand (see Table V); for example, in Id which contains the Me$_2$CHN=C(CH$_3$)C(H)= NCHMe$_2$ ligand we obtained ^{n}J(^{195}Pt-^{13}C) data for the Me$_2$CHN groupings [tertiary C (^{2}J) 24 and 29 Hz and Me (^{3}J) 6 and 6 Hz] as well as for the N=C(CH$_3$) group [CH$_3$(^{3}J) 12 Hz] (see also Figure 3). In [PtCl$_2$(η^2-cis-CH$_3$C$_2$H$_2$CH$_3$)(R-dim)] complexes we found the first examples[23] of a ^{2}J(^{195}Pt-^{13}C) coupling on the imine (C=N) carbon

(23) H. Motschi and P. S. Pregosin, observed a ^{2}J(^{195}Pt-^{13}C) of 13–15 Hz in platinum Schiff-base complexes (*Helv. Chim. Acta.*, in press).
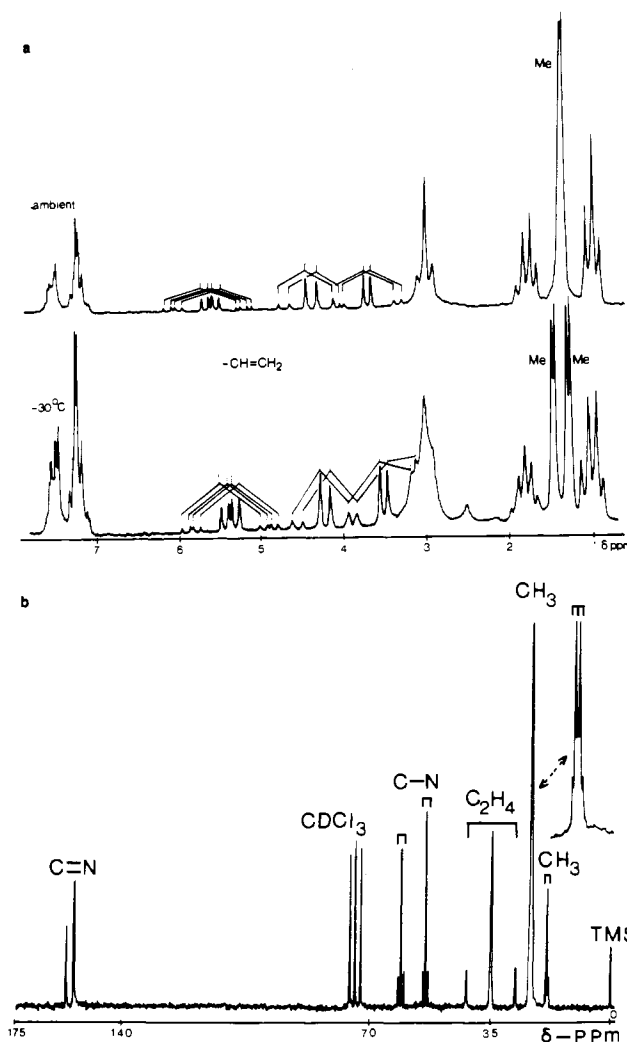
Figure 3. (a) ^{1}H NMR (90 MHz) spectrum of [PtCl$_2$(η^2-styrene)(EtMe$_2$C-diam)]. (b) ^{13}C NMR (20 MHz) spectrum of [PtCl$_2$(η^2-C$_2$H$_4$)(i-Pr-N=C(CH$_3$)C(H)=N-i-Pr)].

(5 Hz). Despite the similar downfield shifts of the imine protons in the four-coordinate V and five-coordinate complexes I–IV (a–d), the ^{3}J(^{195}Pt-^{1}H) coupling ($\sim$40 and $\sim$90 Hz, respectively) is very characteristic for the coordination number

Table IV. ^{1}H NMR^a Spectra of R-dim, R-diam, [PtCl$_2$(R-dim)], [PtX$_2$(η^2-olefin)(R-dim)] and [PtCl$_2$(η^2-olefin)(R-diam)] Complexes

	solvent	CH$_3$	CH$_2$	CH	CH=N	HC=C
		Ligand				
i-Pr-dim	CDCl$_3$	1.24 d		3.43 m	7.93 s	
t-Bu-dim	CDCl$_3$	1.30 s			7.93 s	
EtMe$_2$C-dim	CDCl$_3$	0.85 t, 1.23 s	1.63 q		7.88 s	
t-Bu-diam	CDCl$_3$	1.08 s				
EtMe$_2$C-diam	CDCl$_3$	0.83 t, 1.02 s	1.36 q, 2.57 s			
		Complexes				
[PtCl$_2$(*i*-Pr-dim)]	Me$_2$SO-*d*$_6$	1.40 d		4.87 m	8.77 s (100)	
[PtCl$_2$(*t*-Bu-dim)]	CDCl$_3$	1.80 s			8.67 s (86)	
	Me$_2$SO-*d*$_6$	1.75 s			8.73 s (89)	
[PtCl$_2$(EtMe$_2$C-dim)]	Me$_2$SO-*d*$_6$	0.90 t, 1.67 s	2.37 q		8.82 s (90)	
[PtCl$_2$(η^2-C$_2$H$_4$)(*i*-Pr-dim)]	CDCl$_3$	1.63 d		4.32 m	8.57 s (37)	3.63 s (70)
[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-dim)]	CDCl$_3$	1.67 s			8.68 s (36.5)	3.53 s (71)
[PtBr$_2$(η^2-C$_2$H$_4$)(*t*-Bu-dim)]	acetone-*d*$_6$	1.68 s			8.92 s (37.5)	3.43 s (70)
[PtCl$_2$(η^2-C$_2$H$_4$)(EtMe$_2$C-dim)]	CDCl$_3$	0.91 t, 1.63 s	2.05 q		8.58 s (36)	3.55 s (71)
[PtCl$_2$(η^2-C$_2$H$_4$)(*i*-Pr-NCCH$_3$CHN-*i*-Pr)]	CDCl$_3$	1.57 s, 1.67 s, 2.37 s (5)		4.2 m	8.43 s (40)	3.42 s (68)
[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-diam)]	CDCl$_3$	1.44 s	3.03 s (16)			3.38 s (71)
[PtCl$_2$(η^2-C$_2$H$_4$)(EtMe$_2$C-diam)]	CDCl$_3$	0.83 t, 1.37 s	1.75 q, 3.00 s (16)			3.42 s (70)
[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(*i*-Pr-dim)]	CDCl$_3$	1.68 d		4.73 m	8.63 s (41)	5.67 m (70)
[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	CDCl$_3$	1.60 s			8.80 s (41)	5.22 m (72)
[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]	CDCl$_3$	0.90 t, 1.55 s	1.86 q		8.77 s (41)	5.35 m (72)
[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	CDCl$_3$	1.52 s			8.66 s (41)	5.3 m (62)
[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]	CDCl$_3$	0.87 t, 1.49 s	1.80 q		8.80 s (41)	5.3 m (64)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*i*-Pr-dim)]	CDCl$_3$	1.43 d, 1.52 d		4.10 m	8.47 s (41)	4.04 d (68), 4.64 d (58), 6.07 dd (76)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-dim)]	CDCl$_3$	1.58 s			8.57 s (38)	3.84 d (70), 4.51 d (62), 5.78 dd (82)
	CDCl$_3$^{b}	1.51 s, 1.68 s			8.56 s (41), 8.63 s (35)	3.60 d (70), 4.30 d (63), 5.53 dd (83)
[PtBr$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-dim)]	acetone-*d*$_6$	1.55 s			8.58 s (39.5)	4.07 d (68), 4.77 d (60), 6.13 dd (78)
	acetone-*d*$_6$^{c}	1.39 s, 1.72 s			8.48 s (39), 8.68 s (39)	
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(EtMe$_2$C-dim)]	CDCl$_3$	0.87 t, 1.50 s, 1.57 s	1.87 q		8.57 s (40)	3.97 d (68), 4.60 d (58), 5.90 dd (80)
	acetone-*d*$_6$^{c}	0.66 t, 1.26 s, 1.58 s, 0.77 t, 1.53 s, 1.62 s	1.85 m		8.79 s (41), 8.86 s (37)	3.28 d (70), 4.04 d (61), 5.19 dd (86)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-diam)]	CDCl$_3$	1.35 s	3.04 s (17)			3.60 d (65), 4.30 d (60), 5.53 dd (86)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(EtMe$_2$C-diam)]	CDCl$_3$	0.83 t, 1.22 s, 1.24 s	1.66 q, 2.95 s (17)			3.66 d (62), 4.36 d (54), 5.62 dd (77)
	CDCl$_3$^{d}	0.79 t, 1.12 s, 1.17 s, 0.89 t, 1.31 s, 1.35 s	1.63 q, 2.97 s, 1.75 q			3.48 d (63), 4.22 d (56), 5.41 dd (77)

^{a} Chemical shifts (δ) relative to Me$_4$Si; ^{n}J(^{195}Pt–^{1}H) in parentheses are given in Hz. Key: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet. ^{b} At –28 °C. ^{c} At –50 °C. ^{d} At –25 °C.

of the central platinum atom.

Upon coordination the olefinic H and C atoms NMR resonances exhibit large upfield chemical shifts with respect to the free olefin and are all flanked by ^{195}Pt satellites with sizeable coupling constants. A comparison of the olefinic ^{1}H and ^{13}C NMR data of η^2-olefins in some three-, four-, and five-coordinate platinum complexes with those of the free olefins is given in Table VI. This comparison shows that,
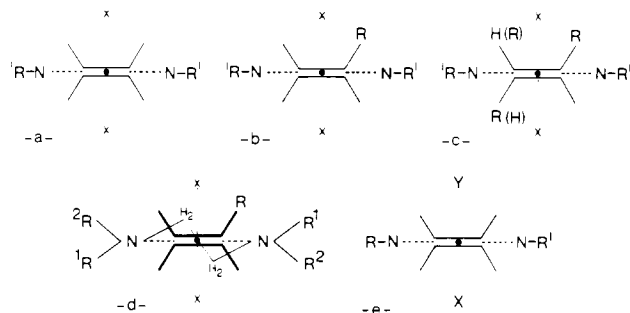
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Figure 4. Ground-state structures: [PtX$_2$(η^2-olefin)(R-dim)] (a, b, c); [PtX$_2$(η^2-olefin)(R-diam)], R^1 $\neq$ R^2 = H (d), [PtX$_2$(η^2-ethene)(6-R-py-2-CH=NR')], x = y (e); [RhCl(CO)(η^2-ethene)-(R-dim)], x = Cl, y = CO, R = R' (e).

particularly in the case of the ethylene and styrene platinum complexes, the magnitude of ^{n}J(^{195}Pt–^{1}H), ^{n}J(^{195}Pt–^{13}C), and the upfield chemical shift of the ^{1}H and ^{13}C resonances are characteristic for the coordination geometry around the central platinum atom. ($\Delta\delta$ 1.7 (^{1}H), $\Delta\delta$ 95 (^{13}C)) with large coupling

Table V. ^{13}C NMR^a Spectra of R-dim, R-diam, [PtCl$_2$(R-dim)], [PtX$_2$(η^2-olefin)(R-dim)], and [PtCl$_2$(η^2-olefin)(R-diam)] Complexes

	solvent	C(H)$_3$	C(H)$_2$	C–N	C=N	C=C
		Ligand				
i-Pr-dim	CDCl$_3$	23.47		60.87	156.46	
t-Bu-dim	CDCl$_3$	28.42		56.94	156.59	
EtMe$_2$C-dim	CDCl$_3$	8.02, 25.97	35.08	60.16	157.85	
t-Bu-diam	CDCl$_3$	28.81	42.97	49.89		
		Complexes				
[PtCl$_2$(*t*-Bu-dim)]	CDCl$_3$–Me$_2$SO	30.13		70.13	164.97	
[PtCl$_2$(η^2-C$_2$H$_4$)(*i*-Pr-dim)]	CDCl$_3$	23.72		63.09 (25)	159.46	38.34 (292)
[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-dim)]	CDCl$_3$	30.60 (3)		64.30 (25)	156.80	38.10 (297)
[PtBr$_2$(η^2-C$_2$H$_4$)(*t*-Bu-dim)]	CDCl$_3$	31.28		64.35 (24)	157.56	35.59 (286)
[PtCl$_2$(η^2-C$_2$H$_4$)(EtMe$_2$C-dim)]	CDCl$_3$	8.76, 27.71	39.18	67.09	157.14	39.18 (293)
[PtCl$_2$(η^2-C$_2$H$_4$)(*i*-Pr-NCCH$_3$CHN-*i*-Pr)]	CDCl$_3$	23.49 (6), 18.80 (12), 23.72 (6)		55.42 (29), 62.84 (24)	162.02, 164.46	35.70 (289)
[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-diam)]	CDCl$_3$	29.25 (6)	43.87 (9)	56.11 (4)		35.71 (298)
[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	CDCl$_3$	30.22		63.23	159.46 (5)	84.06 (177)
	CDCl$_3$^{b}	29.82		63.40	158.24	77.10 (214)
[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]	CDCl$_3$	8.59, 27.48	35.26	66.15 (6)	160.04 (5)	86.07 (169)
	CDCl$_3$^{c}	8.65, 27.14	34.73	66.14	158.98	79.08 (200)
[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	CDCl$_3$	30.36		62.97	160.21	92.07 (160)
	CDCl$_3$^{d}	30.11		63.05	159.61	90.62 (167)
[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(EtMe$_2$C-dim)]	CDCl$_3$	8.62, 27.63	35.42	65.93	160.60	92.44 (166)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*i*-Pr-dim)]	acetone-*d*$_6$	23.41 (br)^h		63.08 (26)	159.72	31.33 (br), 53.77 (br)
	acetone-*d*$_6$^{b}	22.38, 23.51 (br), 23.07		62.89 (25), 63.08 (25)	159.76 (br)	29.05 (303), 50.16 (290)
	CDCl$_3$^{e}	22.57, 23.29, 23.54 23.87		63.70, 63.85	157.11, 157.50	32.75 (br), 54.79 (br)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-dim)]	CDCl$_3$	30.16		63.89 (20)	157.27	40.71 (257), 66.22 (242)
	acetone-*d*$_6$^{f}	29.43, 30.03		63.77 (20), 63.92 (20)	158.59, 158.83	30.47 (296), 51.08 (287)
[PtBr$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-dim)]	CDCl$_3$	30.78		63.93 (18)	158.38	35.87 (br), 68.44 (br)
[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(EtMe$_2$C-dim)]	CDCl$_3$	8.74, 27.22, 27.52	34.92	66.75 (17)	158.09 (5)	44.08, 71.06 (243)
	CDCl$_3$^{g}	8.87, 26.22, 26.55, 9.00, 27.66 (br)	33.94, 34.46	67.06 (18), 67.12 (18)	156.61, 156.73	33.29, 55.66
	acetone-*d*$_6$^{b}	8.46, 25.88, 26.63, 8.67, 27.51, 27.63	33.63, 34.02	66.36 (18), 66.46 (18)	159.11, 159.43	29.59 (306), 50.19 (284)

^{a} Chemical shifts (δ) relative to Me$_4$Si; ^nJ(^{195}Pt–^{13}C) in parentheses are given in Hz. ^{b} At –42 °C. ^{c} At –45 °C. ^{d} At –55 °C. ^{e} At –58 °C. ^{f} At –31 °C. ^{g} At –48 °C. ^{h} br = broad.

Table VI. Olefinic ^{1}H and ^{13}C NMR Data^a of Some Three-, Four-, and Five-Coordinate Platinum–Olefin Complexes

	H$_n$C=	ref	C=C'	ref
C$_2$H$_4$			122.8	22
K[PtCl$_3$(η^2-C$_2$H$_4$)]	4.42 (67)^b	20	71.1 (188),^{c} 67.3 (194)^b	20, 24
trans-[PtCl$_2$(η^2-C$_2$H$_4$)(collidine)]	4.75 (62)	20	75.0 (166)	20
cis-[PtCl$_2$(η^2-C$_2$H$_4$)(Me$_2$SO)]	4.66 (61)	25		
[PtCl(η^2-C$_2$H$_4$)(acac)]	4.44 (65)	26	67.0 (214)	27
trans-[PtCl$_2$(η^2-C$_2$H$_4$)(*t*-Bu-dim)]	3.53 (71)		38.10 (297)	
[PtCH$_3$(η^2-C$_2$H$_4$)(HBPZ$_3$)]	2.14 (69), 2.27 (80)	28	24.7 (384)	28
[Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$]		30	39.6 (194)^d	31
[Pt(η^2-C$_2$H$_4$)$_2$(PPh$_3$)]	2.5 (57)	32	42.3 (146)	32
[Pt(η^2-C$_2$H$_4$)$_2$(PMe$_3$)]	2.7 (57)	32	35.7 (146)	32
C$_2$H$_3$C$_6$H$_5$			112.3, 137.7	22
K[PtCl$_3$(η^2-C$_2$H$_3$C$_6$H$_5$)]	4.30 (69), 4.94 (61), 6.31 (75)^b	23	57.4 (196), 85.6 (172)^b	20
trans-[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(collidine)]		20	62.3 (166), 97.8 (140)	20
[PtCl(η^2-C$_2$H$_3$C$_6$H$_5$)(*N*-Me-*S*-Pro)](R)	4.47 (60), 5.02 (59), 6.45 (66)	29		
[PtCl(η^2-C$_2$H$_3$C$_6$H$_5$)(acac)]			55.7 (221), 87.7 (179)	27
trans-[PtCl$_2$(η^2-C$_2$H$_3$C$_6$H$_5$)(*t*-Bu-dim)]	3.84 (70), 4.51 (62), 5.78 (82)		40.7 (256), 66.22 (242)	
cis-CH$_3$C$_2$H$_2$CH$_3$			123.3	
K[PtCl$_3$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)]	5.06 (67)^b	33	86.9 (175),^{c} 81.3 (184)^b	20, 24
trans-[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(collidine)]	5.20 (60)	33	89.9 (153)	23
[PtCl(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(acac)]	5.36 (75)^b	26		
trans-[PtCl$_2$(η^2-*cis*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	5.22 (72)		84.06 (177)	
trans-CH$_3$C$_2$H$_2$CH$_3$			125.1	
K[PtCl$_3$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)]	4.88 (68)^b	33	89.3 (178)^c	24
trans-[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(collidine)]	5.28 (61)	33	92.52 (155)	
[PtCl(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(acac)]	4.96 (54)	26		
trans-[PtCl$_2$(η^2-*trans*-CH$_3$C$_2$H$_2$CH$_3$)(*t*-Bu-dim)]	5.30 (62)		92.07 (160)	

^{a} ^{1}H and ^{13}C NMR spectra in CDCl$_3$ relative to Me$_4$Si (δ). ^nJ(^{195}Pt–^{1}H) or ^nJ(^{195}Pt–^{13}C) in parentheses are given in Hz. ^{b} In acetone-*d*$_6$. ^{c} In D$_2$O. ^{d} In CD$_2$Cl$_2$.

constants ($^2J(^{195}Pt-^1H) = 71$ Hz, $^1J(^{195}Pt-^{13}C) = 297$ Hz. The value of $^1J(^{195}Pt-^{13}C)$ is the largest of its type yet reported.)

(b) $[PtCl_2(\eta^2\text{-olefin})(R\text{-diam})]$. Comparison of the NMR data for the R-dim and R-diam complexes confirms that the $[PtCl_2(\eta^2\text{-olefin})(R\text{-diam})]$ complexes are likewise five-coordinate species in solution. It is important to note that in the ^1H NMR spectra the N–H resonances were not observed while the N–CH$_2$ resonances appeared fairly broad (vide infra).

(c) Nature of the Dynamic Behavior of $[PtX_2(\eta^2\text{-styrene})(L_2)]$ (L_2 = R-dim or R-diam). Olefin Rotation. Comparison of the ground-state structures in Figure 4 (a, b, and c) reveals that definite conclusions concerning the nature of the dynamics could only be drawn in the case of a monosubstituted olefin in combination with R-dim and R-diam ligands containing a prochiral R group. The monosubstituted olefin (styrene) can coordinate to a platinum center with either one of its two enantiotopic faces. The resulting dissymmetry at the C center connected to the phenyl ring (C_α) can be detected by the prochiral N substituents. Moreover, in the case of rigid olefin rotation (ground state in Figure 4b), the two N substituents become nonequivalent since the olefin resides in the equatorial plane (cf. X-ray structure of $[PtCl_2(\eta^2\text{-styrene})(t\text{-Bu-dim})]$, vide supra]. This assumption for the ground-state geometry in solution (slow-exchange limit) is reasonable since the in-plane olefin conformation has been unambiguously established in CHCl$_3$ for the compounds *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(6\text{-R'-py-2CH}=NR)]$ (two olefin ^{13}C NMR resonances at -50 °C[34] and a-Cl-e-CO-b-($\eta^2\text{-}C_2H_4$)-c,d(R-dim)Rh (AB pattern for the olefinic proton NMR resonances at -50 °C),[35] the latter complex being a five-coordinate Rh^I analogue of *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(R\text{-dim})]$. In these complexes there is a clear distinction between the in-[36] or out-of-plane conformations of the C=C skeleton (see Figure 4e).

^1H and ^{13}C NMR spectra of the $[PtX_2(\eta^2\text{-styrene})L_2]$ complexes are temperature dependent. Below -20 °C all $[PtX_2(\eta^2\text{-styrene})(R\text{-dim})]$ ($R = i$-Pr, t-Bu, EtMe$_2$C) compounds are in the slow-exchange limit. At this temperature, the two RN=CH halves of the R-dim ligand are anisochronous as a result of the dissymmetry in the equatorial plane (see Figure 4). The methyl groups in the prochiral R substituents ($R = i$-Pr, EtMe$_2$C) are diastereotopic, and this was confirmed by the observation of four single resonances for both the Me protons and carbon atoms while the other ^1H and ^{13}C resonances of the R-dim ligand were doubled. In the fast-exchange limit the i-Pr and EtMe$_2$C respective halves should become equivalent and indeed when the temperature is raised this double resonance pattern coalesced into one but the methyl groups remained internally diastereotopic.

In fact the observation that the prochiral groupings NCR$_2$ are diastereotopic over the whole temperature range studied excludes an olefin dissociative–associative process as a possible mechanism for the dynamic behavior. Such a mechanism would result in inversion of the configuration at C_α and therefore render the prochiral groupings in the EtMe$_2$C- and i-Pr-dim ligands homotopic. The observed behavior also excludes the occurrence of intramolecular σ,σN,N' (chelate) $\rightleftarrows$ σN (monodentate) rearrangement of the R-dim ligand via Pt–N bond dissociation–association because this would also

lead to homotopic Me groups. Moreover, such a reversible rearrangment would exert a large influence on the magnitude of the $^nJ(^{195}Pt-^1H)$ and $^nJ(^{195}Pt-^{13}C)$ couplings,[37] which differ considerably in the five- and four-coordinate geometries (see Table IV), and this is clearly not the case. Also in the σN monodentate bonded form, in which the R-dim ligand would adopt a trans conformation, the imine H protons give rise to a four-line pattern[6] while in the σ,σN,N' chelate situation these protons are isochronous. These observations and conclusions indicate that the dynamic behavior of the five-coordinate complexes must relate to rotation of the styrene around the Pt–olefin bond axis. That we are dealing indeed with an example of pure olefin rotation in a five-coordinate geometry (see Discussion) was supported by the ^{195}Pt and ^{15}N NMR[38] spectra of $[PtCl_2(\eta^2\text{-styrene})(t\text{-Bu-dim})]$ (97% ^{15}N enrichment). In the ^{195}Pt NMR spectrum at 34 °C (fast-rotation limit; see ^{13}C NMR data in Table V), we observe a triplet pattern for the X part of an A$_2$X spin system with coupling of ^{195}Pt (X; δ -1996, relative to PtCl$_6^{2-}$) with two isochronous imine ^{15}N (A$_2$) atoms. At low temperature, the imine ^{15}N atoms have become the X part of an ABX spin system resulting in a four-line pattern due to two different $^1J(^{195}Pt-^{15}N)$ couplings.

The R-diam complexes containing both prochiral olefin and N substituents, e.g., $[PtCl_2(\eta^2\text{-styrene})(EtMe_2C\text{-diam})]$, showed resonance patterns characteristic of five-coordinate platinum–olefin complexes and dynamic behavior similar to that of the above discussed R-dim complexes. In particular the observed diastereotopic behavior of the methyl groups in the EtMe$_2$C substituents as well as the nonequivalence of the EtMe$_2$C groupings in the slow exchange establishes that, in these complexes also, neither platinum–olefin dissociation nor platinum–N bond dissociation processes take place on the NMR time scale. Therefore, rotation of the olefin around the Pt–olefin axis also fully accounts for the observed temperature dependence of the ^1H NMR spectra of $[PtCl_2(\eta^2\text{-styrene})(EtMe_2C\text{-diam})]$ (see Table IV).

In contrast to the planar platinum chelate ring in the $[PtX_2(\eta^2\text{-olefin})(R\text{-dim})]$ complexes, the corresponding ring is puckered in the analogous R-diam complexes because of the change in hybridization from sp^2 to sp^3 at both the N and C centers (see Figure 4). This increases the number of possible conformations of the molecules. Moreover, when substituents at each of the N atoms are different (e.g., either H, t-Bu or H, EtMe$_2$C) then σ,σN,N'-chelate-type coordination causes both N atoms to become stable chiral centers. Accordingly, the formation of different diastereomers is expected even when the olefin is achiral. In the first instance, it was surprising that a resonance pattern for $[PtCl_2(\eta^2\text{-styrene})(EtMe_2C\text{-diam})]$ was observed consistent with the presence of only one diastereomer, even though C_α, N$_1$, and N$_2$ are expected to be chiral centers. The possible presence of such diastereomers was reported by De Renzi et al.[18] for $[PtCl_2(\eta^2\text{-olefin})((R,R)\text{-}N,N'\text{-dimethyl-}N,N'\text{-bis}(\alpha\text{-methylbenzyl})\text{-1,2-ethanediamine})]$. Our solution data point either to the unlikely existence of a specific preferred diastereomer in solution or to the occurrence of a process of rapid inversion of configuration

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(35) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta*, in press.

(36) It is worth noting that the asymmetry in the equatorial plane in $[PtCl_2(\eta^2\text{-}C_2H_4)(i\text{-Pr-NC(CH}_3)\text{CHN-}i\text{-Pr})]$ is not reflected in the ^{13}C resonance patterns (see Figure 3, part b). Only one resonance is observed for the olefinic carbon atoms even at -80 °C whereas the i-Pr groupings are anisochronous reflecting the dissymmetry in the R-dim ligand. This may be explained by assuming that the chemical shift difference for the olefinic C atoms could not be resolved.

(37) The ^1H and ^{13}C NMR resonances due to the olefinic unit are flanked by ^{195}Pt satellites over the temperature range studied. Moreover, addition of a twofold excess of styrene or t-Bu-dim ligand to a solution of $[PtCl_2(\eta^2\text{-styrene})(t\text{-Bu-dim})]$ in CDCl$_3$ did not affect the line width, chemical shift positions, or the Pt coupling data of either the free or coordinated styrene and t-Bu-dim ligands in the ^1H NMR spectra. This confirms that olefinic and R-dim exchange is slow on the NMR time scale as we also observed for $[PtCl_2(\eta^2\text{-}C_2H_4)(t\text{-Bu-dim})]$.[11]

(38) At -80 °C when the styrene is in the nonrotation limit, we observed two resonances flanked by platinum satelites ($\delta N_A = 303.0$, $^1J(^{195}Pt-^{15}N_A)$ = 178 Hz; $\delta N_B = 317.7$, $^1J(^{195}Pt-^{15}N_B) = 135$ Hz) and the internal N,N inequivalence is confirmed by the presence of $^nJ(^{15}N_A-^{15}N_B)$ coupling of 5 Hz.[7]

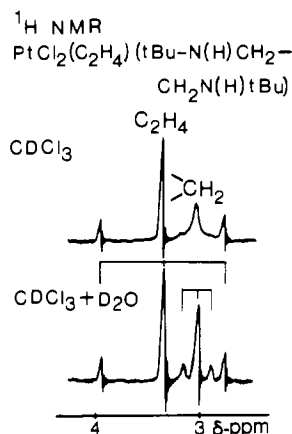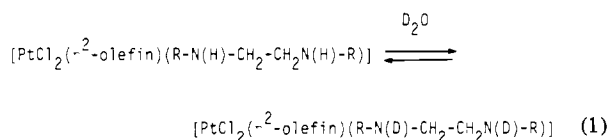**Figure 5.** ^{1}H NMR spectra of [PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-diam)] in CDCl$_3$ (top) and in CDCl$_3$-D$_2$O mixture (bottom).

at the chiral centers. The above mentioned arguments for the absence of Pt–olefin and Pt–N dissociation excluded the C$_\alpha$ atom as being the labile chiral center. However, the absence of the N–H resonance in the ^{1}H NMR in combination with broadened CH$_2$ resonances indicated that rapid inversion at the N centers was possibly the responsible factor.

The NMR spectra of a mixture of [PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-diam)] with D$_2$O in CDCl$_3$ (or acetone-d_6) (see eq 1 and Figure 5) showed the CH$_2$ protons as a sharp singlet flanked

$$\text{[PtCl}_2(\text{-}^2\text{-olefin})(\text{R-N(H)-CH}_2\text{-CH}_2\text{N(H)-R})] \underset{}{\overset{\text{D}_2\text{O}}{\rightleftharpoons}}$$

$$\text{[PtCl}_2(\text{-}^2\text{-olefin})(\text{R-N(D)-CH}_2\text{-CH}_2\text{N(D)-R})] \quad (1)$$

by ^{195}Pt satellites. This appears to be conclusive evidence for H–D exchange at the N centers which would thereby eliminate ${}^3J({}^1$H-^{1}H) couplings between the N–H and CH$_2$ groupings. Furthermore, solutions of this compound after treatment with D$_2$O loose ν(N–H) at 3299 cm^{-1} in their IR spectra while a new absorption is observed at 2389 ν(N–D) cm^{-1}, thus supporting N–H bond dissociation as a route for the inversion of configuration at the N center and the observation of only one isomer.

The combined evidence from the ^{1}H and ^{13}C NMR data and D$_2$O experiments indicates that in five-coordinate [PtCl$_2$(η^2-olefin)(R-diam)] complexes the N–H bond is far more labile than the Pt–N bond. In this context it should be noted that the related four-coordinate [PtCl$_2$(η^2-C$_2$H$_4$)(N-(H)Et$_2$)] complexes have been the subject of H/D experiments by Green et al.[39]

Discussion

During the past few years several five-coordinate platinum–olefin complexes have been isolated. The study of the structure, bonding, and reactivity of these complexes is of interest since they may well serve as models of the five-coordinate intermediates proposed in associative ligand-exchange processes for Pt(II) complexes.[40] We have used our well-defined five-coordinate [PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)] complex for a study of the reactivity of the five-coordinate species toward exchange of the neutral olefin and diimine ligand. In this connection the information presented here concerning the stability of the Pt–olefin and Pt–N,N interaction, the stereochemistry and the nature of the platinum–olefin bonding is

important. These aspects will be discussed in the following sections.

Solution Stability of the Complexes. By far the greatest number of the five-coordinate platinum–arsine, –phosphine,[41] and –olefin[9–11,42] complexes have a trigonal-bipyramidal array similar to that found for [PtCl$_2$(η^2-styrene)(t-Bu-dim)] (Figure 2). Many of these complexes decompose in chlorinated solvents by the loss of the olefin in a single dissociation step producing *cis*-[PtCl$_2$L$_2$].[10,42] From a comparison of the data concerning the solution stability of [PtX$_2$(η^2-ol)L$_2$] complexes known to date,[9,10,42] it is obvious that a systematic rationalization of the factors affecting the stability of these type of five-coordinate species is difficult but some relevant remarks can be made.

In general, Pt^{II}–olefin bonding has been described in terms of the Chatt–Dewar–Duncanson model.[43] This model consists of, first, a σ bond (by combination of the filled π_{2p} orbital of the olefinic (C=C) moiety with the 5d6s6p^2 orbital of the Pt^{II} center) and, second, a π back-bond (from the 5d6p Pt orbital (with b$_2$ symmetry) to the empty π^*_{2p} of the olefinic moiety). The formally empty b$_2$ (5d6p) orbital, which is coplanar with the C=C bond, has the correct geometry to overlap with the antibonding combination of the σ orbitals on the bidentate N,N-ligand. Electron donation from the N–R groups will cause blooming of the b$_2$ orbital toward the olefin and thus enhance the π back-bonding, resulting in a stabilization of the platinum–olefin bond.[13,44]

R-dim and R-diam are good σ-donor ligands, and in our complexes [PtX$_2$(η^2-olefin)L$_2$] solution stability decreases with the decreasing σ-donation ability of R, i.e., EtMe$_2$C, Me$_3$C (C-quarternary) > Me$_2$HC (C-tertiary) >> Ph. The use of weaker electron-releasing ligands like bpy, phen, and butane-2,3-dione R,R'-hydrazone, instead of the R-dim or R-diam, results in complexes which decompose rapidly in solution.[9,42] Panunzi et al.[10] have suggested that in order to obtain stable complexes a moderate bulk must be present at the nitrogen atoms. However, such stabilization could equally be the result of a combination of steric and electronic effects because no correlation could be found between the type of substitution and the stability of the complexes. Whereas [PtCl$_2$(η^2-C$_2$H$_4$)(Me$_2$NCH$_2$CH$_2$NMe$_2$)] decomposes between -10 and 0 °C,[42] [PtCl$_2$(η^2C$_2$H$_4$)(t-Bu-N(H)CH$_2$CH$_2$N(H)-t-Bu)] is stable for 1 week in solution at room temperature.

It is interesting in this respect that we recently observed that the pyridylimine[45] complexes [PtCl$_2$(η^2-olefin)(6-R-py-2-CH=NR')] (see Figure 4c) with R = H generally show solution instability irrespective of the nature of R'. However, in the 6-Me complexes the platinum–olefin bond is stabilized to a considerable extent, and solutions of [PtCl$_2$(η^2-C$_2$H$_4$)(6-Me-py-2-CH=N-CMe$_2$Et)], for example, are stable for several days. Introduction of the 6-Me group enhances the kinetic stability of the five-coordinate Pt–olefin species with respect to the four-coordinate [PtCl$_2$(η^2-C$_2$H$_4$)(6-R-py-2-CH=NR'] species formed by Pt–olefin dissociation.[34]

Olefin Rotation in [PtX$_2$(η^2-styrene)(R-dim)] and [PtCl$_2$-(η^2-styrene)(R-diam)]. The present five-coordinate [PtX$_2$-

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Table VII. Activation Energies of the Barrier to Olefin Rotation

		$\Delta G^{*},^a$ kcal/mol	calcd from $\Delta\delta$	$\Delta G^{*}_{av},^a$ kcal/mol	ref
trans-[PtCl$_2$(η^2-styrene)(*t*-Bu-dim)]	^{1}H NMR	13.75	*t*-Bu	⎫	
		13.85	CH=N	⎬ 13.9	
	^{13}C NMR	14.09	CH=N	⎭	
trans-[PtBr$_2$(η^2-styrene)(*t*-Bu-dim)]	^{1}H NMR	13.15	*t*-Bu	⎫ 13.2	
		13.30	CH=N	⎬	
trans-[PtCl$_2$(η^2-methylacrylate)(*t*-Bu-dim)]	^{1}H NMR	15.91	CH=N	⎫ 15.9	34
	^{13}C NMR	15.82	CH=N	⎬	
trans-[PtCl$_2$(η^2-styrene)(EtMe$_2$C-diam)]	^{1}H NMR	14.58	Me$_2$C–N	14.6	
cis-[PtCl$_2$(η^2-1-butene)(Me$_2$SO)]	^{1}H NMR			14.9	25
cis-[PtCl$_2$(η^2-ethylene)(PEt$_3$)]	^{1}H NMR			12.8	17
cis-[PtCl$_2$(η^2-propene)(PEt$_3$)]	^{1}H NMR			12.8	17
[PtCl(η^2-ethylene)(acac)]	^{1}H NMR			12.5	17
[PtCl(η^2-1,1-diphenylethylene)(acac)]	^{1}H NMR			12.8	17
cis-[PtCl$_2$(η^2-vinyl acetate)(PMe$_2$Ph)]	^{1}H NMR			15.0	46
[Pt^0(η^2-ethylene)$_2$(PMe$_3$)]	^{1}H NMR			13.0	32
[Pt^0(η^2-ethylene)$_2$(PPh$_3$)]	^{1}H NMR			10.2	32

^{a} Calculated according to Lewis et al.[17]

(η^2-olefin)(R-dim)] and [PtCl$_2$(η^2-olefin)(R-diam)] complexes complete the series: trigonal Pt^0–olefin, square-planar Pt^{II}–olefin, and trigonal-bipyramidal Pt^{II}–olefin complexes. Experimental evidence from the complexes [Pt^0(η^2-olefin)L$_2$] and [Pt^{II}(η^2-olefin)L$_3$] consistently shows the olefin orientated coplanar with Pt^0 and perpendicular to the coordination plane of Pt^{II}, respectively. The [PtX$_2$(η^2-olefin)L] complexes reported in this paper contain the olefin in the equatorial plane, in agreement with the available structural data from other five-coordinate olefin–metal complexes. Extensive studies have been carried out by Lewis et al. on the elucidation of the factors governing the barrier to olefin rotation in square-planar Pt^{II} complexes,[17] and more recently Stone et al. have made similar studies on [Pt^0(η^2-olefin)$_2$L] complexes.[32] To date, however, no analysis of the olefin rotation barrier in five-coordinate [PtX$_2$(η^2-olefin)L$_2$] species had been carried out. We now report, in Table VII, the activation energies of the barrier to olefin rotation (ΔG^{*}) in various complexes of this type.

It is worth noting that the activation energies of the five-coordinate [PtX$_2$(η^2-olefin)L$_2$] were derived from the $\Delta\delta$ of various nuclei in the R-dim or R-diam ligands. In the studies of the [Pt^0(η^2-olefin)$_2$L] and [Pt^{II}(η^2-olefin)LX$_2$] complexes, calculations were carried out with the use of $\Delta\delta$ of the olefinic ^{13}C or ^{1}H resonances. The very small differences in the values calculated from the ^{1}H or ^{13}C NMR spectra of the present five-coordinate Pt^{II} complexes give confidence in their accuracy. The ΔG^{*} values fall in the same range as those for four-coordinate *cis*-[Pt^{II}X$_2$(η^2-olefin)L] and [Pt^{II}X(η^2-olefin)L$_2$] and three-coordinate [Pt^0(η^2-olefin)$_2$L] complexes (see Table VII, as well as many other five-coordinate species, e.g., [Fe(CO)$_4$(η^2-olefin)] (10–16 kcal/mol)[12] and [RhX$_2$(RC≡N)$_2$(η^2-olefin)] (10–18 kcal/mol).[47]

In their paper concerned with the activation barrier to olefin rotation in ethene–ML$_{2-5}$ species, Hoffman et al.[12] note the remarkable resemblance between the valence orbitals of the Ni^0(CO)$_2$ and Fe^0(CO)$_4$ fragments, which suggested a similar interaction between the metal (Ni^0, Fe^0) and the olefin ligand in the respective olefin complexes. The important factors determining the barrier to olefin rotation in the corresponding [Ni^0(CO)$_2$(η^2-olefin)] and [Fe^0(CO)$_4$(η^2-olefin)] complexes appeared to be the degree of bending back of the groups connected to the C=C moiety of the olefin. Additionally, for the five-coordinate Fe^0 complexes, the barrier to distortion of the trigonal-bipyramidal geometry toward a square-pyramidal geometry had to be added. On this basis the calculated barriers for the trigonal [M(η^2-olefin)$_{3-n}$L$_n$] complexes (pure

olefin rotation) and the five-coordinated [Fe(CO)$_4$(η^2-C$_2$H$_4$)] (concerted olefin rotation/Berry pseudorotation or turnstile processes) were found to be similar, in agreement with experimental results.[48]

It is obvious that the five-coordinate [Fe(CO)$_4$(η^2-olefin)] species are isoelectronic (18e) with our five-coordinate [PtX$_2$(η^2-olefin)L$_2$] complexes. In these platinum(II) complexes, each of the ligands has a strong preference for a particular site in the trigonal-bipyramidal array; the electronegative halogen atoms for the axial and the σ,σN,N'-bonded R-dim and R-diam ligands for the equatorial sites trans to the olefin (vide supra). In this respect the connectivity of the bidentate ligand is of importance, preventing stereoisomers with axial-positioned N atoms. We have never found evidence for the existence of other stereoisomers on the NMR time scale. In our system, therefore, the occurrence of Berry pseudorotation (or turnstile) processes is unlikely because such processes would involve the formation of other unfavorable stereoisomers as intermediates. Accordingly, the observed barriers to rotation in [PtX$_2$(η^2-olefin)L$_2$] (15 kcal/mol) almost certainly only correspond to the occurrence of pure olefin rotation about the platinum–olefin axis. It seems plausible to assume that, in the upright olefin conformation, bending back of the halogen atoms occurs; i.e., the Cl-Pt-Cl angle which is 179.3° in the solid (vide supra) becomes smaller in order to minimize the steric interaction between the olefin and the Cl atoms.

The energy for this distortion is expected to be independent of whether Br or Cl is present at the axial sites. The almost similar ΔG^{*} values of Br and Cl analogues in both five- and four-coordinate[17] Pt–olefin complexes confirms this hypothesis. In this respect it is interesting to mention the results of calculations by Hoffmann et al.[12] concerning the influence of bending back of the ligands cis to the olefin in square-planar *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(PH$_3$)] and *trans*-[PtH(η^2-C$_2$H$_4$)(PH$_3$)$_2$] on the ΔG^{*} values for the olefin rotation barriers. It appeared that the ΔG^{*} values 27 and 5 kcal/mol, respectively, are strongly dependent on the bulkiness of the ligand trans to the olefin and accordingly cis to the atoms which are bent back. In the *trans*-[PtX$_2$(η^2-olefin)(R-dim)] complexes, the NCCN skeleton of the R-dim ligand is extended exclusively in the equatorial plane and thus can be considered to be a trans ligand with minimal steric bulk with respect to the cis-positioned halogen atoms (see Figure 6). The slightly higher ΔG^{*} value

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(48) It might well be that the high value of 39 kcal/mol calculated for the pure olefin-rotation process in [Fe(CO)$_4$(η^2-olefin)] (**12**) lowers to the experimentally found values of 10–15 kcal/mol when a simple bending back of the axial CO ligands is included.
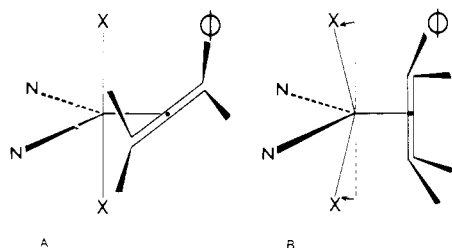
Figure 6. Back bending of the axial ligands in the upright conformation of the styrene molecule in [PtX₂(η²-styrene)(R-dim)] complexes during the olefin-rotation process.

found for the corresponding R-diam ligand is in agreement with this model since the puckering in the five-membered chelate ring (see Figure 4d) should give rise to slightly increased steric bulk toward the Cl–Pt–Cl distortion. In accord with this line of argumentation is the observation that the ΔG^* values of our trigonal-bipyramidal [PtX₂(η²-olefin)L₂] are fully comparable with those of square-planar [PtX₃₋ₙ(η²-olefin)Lₙ].

Conclusions

The present results show that five-coordinate platinum-(II)–olefin complexes of the type [PtCl₂(η²-olefin)L₂] (L = R-dim, R-diam) are stable when the N–R group has good σ-donating properties. The equatorial plane of the trigonal-bipyramidal array contains both the olefinic skeleton and the two N-donor atoms of the bidentate ligand. On the basis of the Chatt–Dewar–Duncanson olefin–metal bonding scheme, increased σ donation from the bidentate ligand to the platinum center enhances back-bonding from this center to the olefin, thereby increasing the strength of the platinum–olefin interaction. It has been shown with use of ¹H, ¹³C, ¹⁵N, and ¹⁹⁵Pt NMR spectroscopy on nonlabeled and ¹⁵N labeled complexes that the dynamic process observed is due to the occurrence of pure olefin rotation around the platinum–olefin axis. The data exclude the occurrence of Berry pseudorotation (or turnstile) processes in concert with the rotation process on the NMR time scales.

An X-ray structure determination of [PtCl₂(η²-styrene)(t-Bu-dim)] revealed that the degree of bending back of the

substituent connected to the C=C moiety (27°) is in the range observed for a large series of metal–η²-olefin complexes.

The observed barrier to rotation of the olefin for the complexes is low (14–15 kcal/mol) as compared with the barrier of 30 kcal/mol obtained from theoretical calculations for pure olefin rotation (without concerted stereoisomerization processes) but in the range of the barrier found for square-planar [PtX(η²-olefin)L₂] complexes. This is explained by a bending back of the axially positioned halogen atoms in the trigonal-bipyramidal array when the olefin passes the upright conformation during the rotation. The bending back of the halogen atoms, which thus move toward the chelate bonded L₂ ligand in the equatorial plane is determined by the steric constraints of this L₂ ligand. The α-diimine ligand which is extended exclusively in the equatorial plane can be considered to be a ligand with minimal steric bulk. The diamino ligands are expected to give rise to somewhat higher barrier to rotation because they exert a larger steric influence on the axial ligand resulting from the puckered five-membered chelate rings.

Five-Coordinate Platinum–Olefin Complexes. Synthesis and High-Resolution ¹H (250, 360 MHz) and ¹³C (20 MHz) NMR Study of the Interligand Chiral Recognition in the Formation of Diastereomeric [PtCl₂(η²-olefin)(6-R′-py-2-CH=NR)]

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Five-coordinate platinum(II)–olefin complexes of the type [PtCl₂(η²-olefin)(6-R′-pyridine-2-carbaldehyde imine)] were obtained from the 1/1 molar reaction of K[PtCl₃(η²-olefin)] with 6-R′-pyridine-2-carbaldehyde imine in acetone or methanol. On the basis of the ¹H and ¹³C NMR data (characteristic ¹H and ¹³C chemical shifts and ⁿJ(¹⁹⁵Pt–¹H), ⁿJ(¹⁹⁵Pt–¹³C) values), a trigonal-bipyramidal structure is proposed for these complexes in solution. The Cl atoms occupy the axial sites while the 6-R′-pyridine-2-carbaldehyde imine ligand and olefin reside in the equatorial plane. The ¹H (60, 100, 250, and 360 MHz) and ¹³C (20 MHz) NMR spectra of these complexes excluded the occurrence of Pt–N and Pt–olefin bond dissociation/association processes, and temperature-dependent spectra pointed to pure rotation of the olefin around the platinum–olefin bond axis. In the ethylene species, the latter process was detectable owing to the existence of asymmetry in the equatorial plane resulting from the pyridylimine skeleton. Moreover the observation of anisochronous olefinic ¹³C resonances in the slow-exchange limit revealed unambiguously that in solution the C=C unit in the ground-state structures of five-coordinate platinum–olefin complexes adopts an in-plane equatorial conformation.

Introduction

Extensive studies have been carried out directed at elucidation of the factors which control diastereotopic discrimi-

nation during metal–olefin bond formation between a prochiral olefin and a metal complex containing either a chiral metal center or a chiral coligand. Understanding of this diastereo-