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-bipyrimidal 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)]

HENK van der POEL and GERARD van KOTEN*

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 ⁿ*J*(¹⁹⁵Pt–¹H), ⁿ*J*(¹⁹⁵Pt–¹³C) values), a trigonal-bipyrimidal 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-
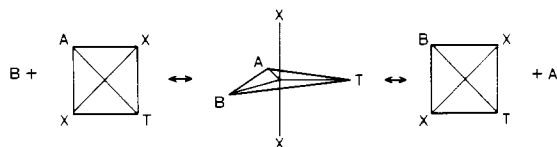
Figure 1. S_N2 mechanism for substitution reactions in square-planar four-coordinate complexes.

topic interaction, as well as the ability to control this, is of great importance for designing catalytic processes involving conversion of prochiral olefins with a high degree of asymmetric induction. With regard to this problem, knowledge about the interaction of olefins with platinum(II) complexes is of crucial importance and has been the subject of a large number of reports.[1–3]

It is generally believed that ligand substitution reactions in square-planar four-coordinated *trans*-[PtX₂AT] (see Figure 1) complexes occur via five-coordinate intermediates which have trigonal-bipyramidal structures, with the actual exchange taking place in the trigonal plane. The exchange of ligand A for B occurs with retention of the transorientation of the X ligands, i.e., the ligands which are cis positioned with respect to [T] in the square-planar structure and which occupy the axial sites in the trigonal-bipyramidal intermediate.[4] This means that during the exchange the actual stereochemistry of the complexes differs. Accordingly, it might be anticipated that the degree of diastereotopic discrimination, which depends strongly on the configuration of the metal center and coligands, is different in each of these intermediates.

Recently we reported the synthesis, characterization, and molecular dynamics of [PtX₂(η²-olefin)(R-dim)] and [PtX₂-(η²-olefin)(R-diam)] complexes which, according to X-ray diffraction analysis of [PtCl₂(η²-styrene)(*t*-Bu-NCHCHN-*t*-Bu)], have a five-coordinate structure in the solid state.[5,6] In this structure the chloro atoms reside at the axial positions, while the olefin and the σ,σN,N′-bonded R-dim ligand occupy the equatorial coordination sites. Extensive ¹H, ¹³C, ¹⁵N, and ¹⁹⁵Pt NMR spectroscopic studies revealed that these structural features are also retained in solution. For the first time it was possible in these types of five-coordinate complexes to study olefin rotation about the platinum–olefin bond axis. Furthermore, halogen–halogen exchange and ligand substitution reactions with olefins, α-diimines (=R-dim), pyridines and N,N′-disubstituted 1,2-diaminoethanes (=R-diam) were observed in [PtCl₂(η²-C₂H₄)(*t*-Bu-dim)] with retention of the five-coordinate array around the platinum(II) center.[7] A dissociative/associative mechanism involving breaking of one of the platinum–N bonds of the σ,σN,N′ chelate bonded R-dim ligand, resulting in a four-coordinate intermediate containing a monodentate σN-bonded R-dim ligand, has been proposed for these substitution reactions.[7]

On the basis of these results, we modified the stable [PtCl₂(η²-olefin)(R-dim)] complexes into [PtCl₂(η²-olefin)-(6-R′-py-2-CH=NR)] complexes which can be utilized as suitable models for the study of the interligand recognition in five-coordinate platinum–olefin species. In these complexes the trigonal equatorial plane is asymmetric (because the two N ligand sites are no longer equivalent) as was not the case in the [PtCl₂(η²-olefin)(RNCHCHNR)] complexes. The

diastereomeric discrimination during the formation of the [PtCl₂(η²-olefin)(6-R′-py-2-CH=NR)] (prochiral olefin) has been studied by using 6-R′-pyridine-2-carbaldehyde imine ligands in which R is (S)-CH(CH₃)Ph. Moreover, variable-temperature ¹H and ¹³C NMR spectroscopic studies have revealed information about aspects of olefin rotation or oscillation and rotamer distribution in the two diastereomers.

Experimental Section

Preparation of Compounds. The 6-R′-pyridine-2-carbaldehyde imines (R = H or Me) were prepared via 1:1 molar ratio condensation reactions of 6-R′-pyridine-2-carbaldehyde and the corresponding primary amines. Relevant ¹H and ¹³C NMR data are given in Tables II and III. The starting complexes K[PtCl₃(η²-C₂H₄)]·H₂O (Zeise's salt) and its styrene analogue were prepared by methods described elsewhere.[8] The preparations of new metal complexes were carried out in a N₂-atmosphere; solvents were purified and distilled before use.

trans-[PtCl₂(η²-olefin)(6-R′-py-2-CH=NR)] (Olefin = Ethylene, Styrene, R¹ = H, CH₃; R = *i*-Pr, *t*-Bu, CMe₂Et). 6-R′-py-2-CH=NR (1.1 mmol) was added to a stirred solution of Zeise's salt (or analogue) (1 mmol) in acetone (10 mL). After 5 min of stirring, the solution was filtered through a short layer of Celite to remove the KCl formed and other trace impurities. The filtrate was concentrated until dry (25 °C) and the residue washed with hexane (3 × 10 mL) and dried in vacuo, resulting in yellow crystalline products. When necessary, the 6-Me derivatives were further purified by recrystallization from a dichloromethane/hexane mixture; yield 70–90%.

trans-[PtCl₂(η²-olefin)(6-R′-py-2-CH=NR)] (Olefin = Ethylene, Styrene; R′ = H, CH₃; R = (S)-C(H)Me)Ph, Ph₂C(H)). 6-R′-py-2-CH=NR (1.1 mmol) was added to a saturated solution of Zeise's salt (or the styrene analogue) (1 mmol) in methanol at 0 °C. Within a few minutes the product precipitated from the solution. The yellow solid was filtered off, washed with hexane (3 × 10 mL), and then dried in vacuo. The 6-Me derivatives could be purified by recrystallization from a dichloromethane/hexane mixture (–20 °C); yield 60–80%.

Physical Measurements. Microanalyses were performed by W. J. Buis of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands. Molecular weights were measured in chloroform (34 °C) with use of a 302 B Hewlett-Packard vapor pressure osmometer. ¹H NMR spectra were recorded variously on Varian T-60/XL-100 and Bruker 250/360 MHz spectrometers with tetramethylsilane (Me₄Si) or CHCl₃ as internal standard. ¹³C NMR spectra were obtained on a Varian CFT-20 using chloroform-*d* as internal standard. 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 2S Raman spectrophotometer as the pure solid.

Results

The 1:1 molar reactions of Zeise's salt (K[PtCl₃(η²–olefin)]; olefin = ethylene or styrene) with 6-R′-py-2-CH=NR (R′ = H or CH₃; R = *t*-Bu, EtMe₂C, (S)-C(H)(Me)Ph, Ph₂C(H), or *i*-Pr) in acetone or methanol afforded stable yellow solids. According to elemental analyses, these solids have [PtCl₂-(η²–olefin)(6-R′-py-2-CH=NR)] stoichiometry. Molecular weight determinations by osmometry revealed that these complexes exist as monomers in chloroform (for analytical data, see Table I). The complexes have good solubility in common organic solvents while in various cases the stability in solution was sufficient to allow recording of their ¹³C NMR spectra both at +34 and –55 °C. In general the 6-methyl-substituted derivatives 6-Mepy-2-CH=NR appeared to be more stable with respect to olefin–platinum bond dissociation (see eq 1) than the unsubstituted compounds. Replacement

(1) Paiaro, G. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 319–335.
(2) Jensen, H. P.; Woldbye, R. *Coord. Chem. Rev.* **1979**, *29*, 213–235.
(3) Müller-Bamert, A. G. Ph.D. Thesis, ETH, Zürich, 1979.
(4) Hupp, S. S.; Dahlgren, G. *Inorg. Chem.* **1976**, *15*, 2349–2353.
(5) van der Poel, H.; van Koten, G.; Vrieze, K.; Kokkes, M.; Stam, C. H. *J. Organomet. Chem.* **1979**, *175*, C21–C24.
(6) van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.*, preceding paper in this issue.
(7) van der Poel, H.; van Koten, G. *J. Organomet. Chem.* **1980**, *187*, C17–C21.

$$K[PtCl_3(\eta^2\text{-olefin})] + L_2 \underset{-KCl}{\overset{}{\longrightarrow}} [PtCl_2(\eta^2\text{-olefin})L_2] \overset{\Delta t}{\longrightarrow} [PtCl_2]_2 + \text{olefin}$$

olefin: ethene, styrene

$$\tag{1}$$

L_2 = 6R′-py-2CH=N-R; R′=H, R=t-Bu,S-C(H)(Me)Ph

R′=Me, R=i-Pr,EtMe₂C-,Ph₂C(H)-,S-C(H)(Me)Ph

(8) Orchin, M.; Schmidt, P. J. *Inorg. Chim. Acta Rev.* **1968**, 123–135.
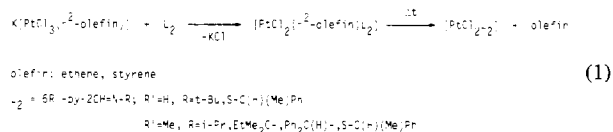
Table I. Analytical Data

	%C found	%C calcd	%H found	%H calcd	%Cl found	%Cl calcd	%N found	%N calcd	mol wt found	mol wt calcd	$T_i{}^a$	$T_f{}^b$
[PtCl$_2$(py-2-CH=N-t-Bu)]	28.28	28.05	3.05	3.29			6.06	6.54				
[PtCl$_2$(py-2-CH=NC(H)(Me)Ph)]^c	38.05	37.51	3.23	3.15	15.25	15.82	6.53	6.25				
[PtCl$_2$(η^2-C$_2$H$_4$)(py-2-CH=N-t-Bu)]											98	147
[PtCl$_2$(η^2-C$_2$H$_4$)(py-2-CH=N-C(H)(Me)Ph)]^c											66	75
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(Me)$_2$Et)]	34.52	34.72	4.50	4.58	14.39	14.64	5.82	5.78			140	188
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)(Me)Ph)]^c	38.94	39.31	3.82	4.08	13.96	13.65	5.40	5.39	493	519.4	130	145
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(Me)$_2$Et)]	42.05	42.85	4.89	4.68	12.16	12.65	5.21	5.00	584	560.4		
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(H)(Me)Ph)]^c	46.06	46.39	4.12	4.23	12.69	11.91	4.59	4.70	576	595.5	82	102

^{a} Initial temperature for decomposition in °C. Determined by thermogravimetric measurements. ^{b} Final temperature (°C). ^{c} The nitrogen C atom has the S configuration.

of the t-Bu or CMe$_2$Et groups by the (S)-C(H)(Me)Ph substituent decreased the solution stability considerably. For example, in the case of [PtCl$_2$(η^2-ethylene)(py-2-CH=NC-(H)(Me)Ph], decomposition in CDCl$_3$ solution was complete within 1 h.[9,10]

According to thermographic analyses, no melting points were observed but the solid compounds [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] did decompose on heating by release of the olefin[9,10] (detected by GLC), affording the square-planar cis-[PtCl$_2$(6-R'-py-2-CH=NR)] complexes. These four-coordinate complexes were identified by comparison of their ^{1}H NMR and IR data with authentic samples (see Tables II and IV). We failed to synthesize [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] by the reverse reaction, i.e., by reacting cis-[PtCl$_2$(6-R'-py-2-CH=NR)] with the appropriate olefin in solution (25 °C at 50 atm in case of C$_2$H$_4$). In contrast to the reversibility of the ligand-exchange reaction of [PtCl$_2$-(η^2-C$_2$H$_4$)(t-Bu-dim)] with the bidentate R-dim and R-diam ligands, the substitution reaction with 6-R'-py-2-CH=NR ligands is irreversible. The failure to exchange the olefin in the [PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NCMe$_2$Et)] complexes (e.g., with maleic anhydride or methyl acrylate) suggests that the change in coordination mode from a σ,σN,N' to σN monodentate, which is a prerequisite for the substitution of either the olefin or the R-dim (R-diam) ligand, apparently cannot occur in the case of the 6-R'-py-2-CH=NR ligand.[7,11]

Structural Characterization and Dynamic Behavior (Olefin Rotation) of the Five-Coordinate [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] Complexes. ^{1}H and ^{13}C NMR data of the monomeric [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] complexes are presented in Tables II and III. These data reveal that upon coordination the 6-R'-py-2-CH=NR ligand resonances undergo a considerable downfield shift. The σ,σN,N' chelating behavior of this ligand is indicated by the observation of ^nJ-(^{195}Pt–^{1}H) and ^nJ(^{195}Pt–^{13}C) couplings (on H and C nuclei, respectively) within the pyridine and substituted imine part of the ligand. That the complexes are five-coordinate species can indeed be deduced from the observation for the imine proton of characteristic ^3J(^{195}Pt–^{1}H) values of ca. 40 Hz which are in the range generally found for the five-coordinate [PtCl$_2$(η^2-olefin)(R-dim)] complexes.[6] It is interesting that in the four-coordinate [PtCl$_2$(6-R'-py-2-CH=NR)] complexes the ^3J(^{195}Pt–^{1}H) value is ca. 100 Hz, comparable with the range of 90–100 Hz found for square-planar [PtCl$_2$(R-dim)] complexes.[6] Further evidence for five-coordination about the platinum center in these complexes comes from the characteristic large upfield shifts of the η^2-coordinate olefin proton ($\sim$3.5 ppm) and carbon ($\sim$40 ppm) resonances which are
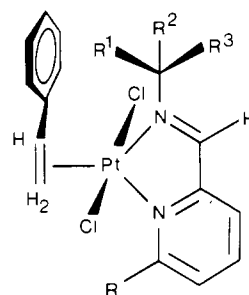

Figure 2. Proposed molecular geometry of [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] complexes.

moreover flanked by platinum satellites with the cooresponding large ^2J(^{195}Pt–^{1}H) ($\sim$70 Hz) and ^1J(^{195}Pt–^{13}C) ($\sim$300 Hz) values.[6]

The trans position of the Cl atoms in the structure was shown by the platinum–halogen stretching modes in the IR and Raman spectra of the complexes (for data see Table IV). On the basis of these data and in analogy with the five-coordinate structure established for the [PtCl$_2$(η^2-styrene)(t-Bu-dim)] compound,[5,6] these 6-R'-py-2-CH=NR complexes have a similar trigonal-bipyramidal structure. The halogen atoms occupy the axial positions, and the olefin and the 6-R'-py-2-CH=NR ligand reside in the equatorial plane (see Figure 2) while in solution occurrence of rotation (or oscillation) of the olefin around the platinum–olefin bond axis can be anticipated. In the five-coordinate ethylene complexes, the ^{1}H NMR spectra can not provide conclusive information about whether the ethylene resides in the upright or in-plane conformation in the ground state (slow-exchange limit). In both conformations the prochiral olefinic protons become diastereotopic because of the bidentate N-donor ligand asymmetry in the equatorial plane. Depending on the type of imino substituent R, for both conformations, either an AA'BB' (R = i-Pr, t-Bu, EtMe$_2$C, Ph$_2$C(H)) or an ABCD (R = (S)-PhCH(CH$_3$)) pattern is expected. Since for all these complexes the 60-MHz ^{1}H NMR spectra revealed only one singlet ethylene resonance flanked by Pt satellites over the temperature range −55 to +34 °C, the complexes were studied at 250 and 360 MHz. Under these high-field conditions, [PtCl$_2$-(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NR)] (R = i-Pr, EtMe$_2$C) did indeed show an AA'BB' pattern for the olefinic protons (25 °C, 250 MHz) with $\Delta\nu_{AB}$ of ca. 8 and ca. 25 Hz, respectively. In the case of R = Ph$_2$C(H), a very broad resonance was observed at 25 °C (250 MHz) which split into an AB pattern in the slow-exchange limit (−55 °C; $\Delta\nu_{AB}$ = 65 Hz).

The ^{13}C NMR (20-MHz) spectra of all the ethylene complexes recorded at −55 °C showed two olefinic C resonances flanked by ^{195}Pt satellites (see Table III). This indicates that at this temperature the ethylene molecule resides in the equatorial plane (see Figure 2) because only in this in-plane conformation are the two C atoms anisochronous. In the

(9) (a) Maresca, L.; Natile, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1140–1142. (b) Maresca, L.; Natile, G.; Rizzardi, G. *Inorg. Chim. Acta* **1980**, *38*, 137–139.

(10) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549–554.

(11) van der Poel, H.; van Koten, G. *J. Chem. Soc., Dalton Trans.*, in press.

Table II. ^{1}H NMR Spectra^a of 6-R'-py-2-CH=N-R, [PtCl$_2$(py-2-CH=NR)], and [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)]

compds	T, °C	MHz	CH$_3$	CH (or CH$_2$)	N=CH	6-R'-py (R = H, CH$_3$)	C$_2$H$_4$ or C$_2$H$_3$Ph
6-Hpy-2-CH=N-t-Bu	+34	60	1.28 s		8.25 s	8.52 d	
cis-[PtCl$_2$(6-Hpy-2-CH=N-t-Bu)]	−36	100	1.47 s		8.62 (102) s	9.47 (36) d^b	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Hpy-2-CH=N-t-Bu)]	+34	100	1.66 s		8.81 (35) s	9.30 (14) d^b	3.51 (71) s
6-Hpy-2-CH=NC(H)(Me)Ph^j	+34	60	1.60 d	4.60 q	8.35 s	8.51 d	
cis-[PtCl$_2$(6-Hpy-2-CH=NC(H)(Me)Ph)]^j	−35	100	1.72 d	6.14 q	8.30 (100) s	9.48 (38) d^b	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Hpy-2-CH=NC(H)(Me)Ph)]^j	−55	100	1.80 d	5.4 m	8.46 (39) s	9.75 (15) d^b	3.42 (69) s
6-Mepy-2-CH=NC(H)Me$_2$	+34	60	1.23 d	3.60 sept	8.28 s	2.53 s	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)Me$_2$)]	+25	250	1.66 d	4.26 sept	8.82 (38) s	3.17 s [3.17 (6) s]^c	3.48 (71)^d [3.46 (68) s]
6-Mepy-2-CH=NC(H)Ph$_2$	+34	60		5.63 s	8.45 s	2.52 s	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)Ph$_2$)]	−55	250		6.67 d^e [6.73 (5) d^e]^f	8.38 d^e [8.47 (38) d]^c	3.16 s [3.17 (8) s]^c	3.12^g [3.12 br (25 °C)] [3.16 (70) s]^c
6-Mepy-2-CH=NC(Me)$_2$Et	+34	60	0.83 t, 1.23 s	1.60 q (CH$_2$)	8.22	2.53 s	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(Me)$_2$Et)]	+25	250	0.87 t, 1.62 s	2.09 q (CH$_2$)	8.69 (35) s	3.17 s [3.17 (7) s]^c	3.55^h [3.48 (70) s]^c
6-Mepy-2-CH=NC(H)(Me)Ph^j	+34	60	1.57 d	4.58 q	8.38 s	2.53 s	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)(Me)Ph)]^j	+25	360	2.14 d	5.43 d of q^e	8.59 d^e [8.40 (37) d^e]^c	3.16 s [3.15 (6) s]^c	3.4 (70) s [3.41 m (−80 °C)]^c
[PtCl$_2$(η^2-styrene)(6-Mepy-2-CH=NC(H)Me$_2$)]	+25	250	1.64 d, 1.98 d	4.4 m	8.63 s	3.46 s	3.75 d, 4.41 d, 5.60 dd^k
			2.00 d, 2.04 d	4.4 m	8.72 s	3.28 s	3.88 d, 4.46 d, 5.48 dd
					9.37 s	3.55 s	3.97 d, 4.72 d, 5.80 dd
[PtCl$_2$(η^2-styrene)(6-Mepy-2-CH=NC(Me)$_2$Et)]	+25	360	0.87 t, 1.49 s, 1.73 s	2.04 m (CH$_2$), 2.13 m (CH$_2$)	9.48 s	3.32 s	3.90 d, 4.61 d, 5.91 dd
			1.00 t, 1.80 s, 1.86 s	2.32 m (CH$_2$)			
[PtCl$_2$(η^2-styrene)(6-Mepy-2-CH=NC(H)(Me)Ph)]^j	+25	360	2.28 d	5.78 m, 5.93 m	8.74 s, 8.84 s	3.41 s	3.79 d, 4.55 d, 5.93 m
			1.80 d	6.09 q	9.01 s	3.16 s, 3.22 s	3.68 d, 4.52 d, 5.78 m

^{a} In chloroform-d. Me$_4$Si is used as standard (ppm); $^nJ(^{195}$Pt–^{1}H) couplings in brackets are given in Hz. ^{b} $^3J(^1$H–^{1}H) ≈ 5 Hz. ^{c} From 60-MHz spectrum. ^{d} AA'BB' pattern, Δδ$_{AB}$ ≈ 8 Hz. ^{e} $^4J(^1$H–^{1}H) = 2 Hz. ^{f} From 100-MHz spectrum. ^{g} AA'BB' pattern, Δδ$_{AB}$ ≈ 65 Hz. ^{h} AA'BB' pattern, Δδ$_{AB}$ ≈ 25 Hz. ^{i} From 250-MHz spectrum. ^{j} The nitrogen C atom has the (S) configuration. ^{k} dd is doublet of doublets.
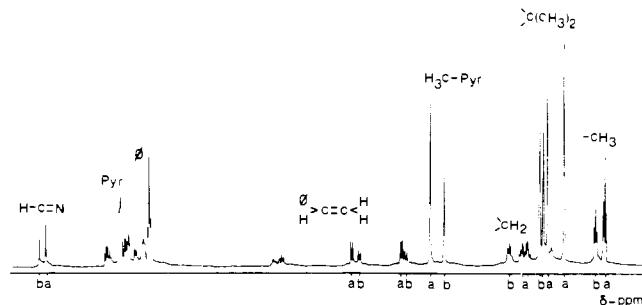

Figure 3. ^{1}H NMR (360-MHz) spectrum of [PtCl$_2$(η^2-styrene)(6-Mepy-2-CH=NCMe$_2$Et)] showing two patterns of rotamers a and b, respectively.
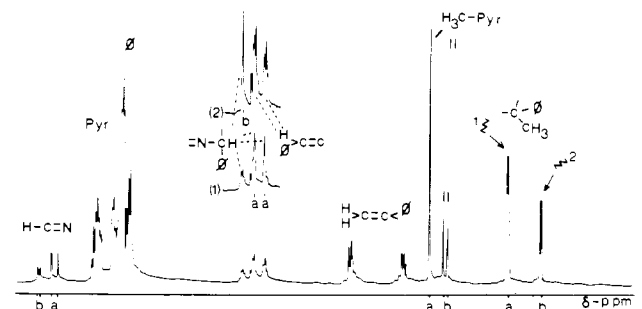

Figure 4. ^{1}H NMR (360-MHz) spectrum of [PtCl$_2$(η^2styrene)(6-Mepy-2-CH=N-(S)-CH(CH$_3$)(Ph))] showing the four patterns arising from the two diastereomers each in a pair of rotamers (a and b).

upright olefin conformation the C atoms are isochronous and only one olefinic C resonance is to be expected. For the complexes with R' = Me and R = *i*-Pr or EtMe$_2$C, the ^{13}C NMR pattern showed two olefinic resonances which remained unchanged up to 34 °C. Recording of the spectra at even higher temperatures, in order to reach the fast-exchange limit, was not possible because of the thermal instability of these solutions. In the two other cases, i.e., R' = H, R = *t*-Bu and R' = Me, R = PhCH(CH$_3$), the two olefinic C resonances observed at −55 °C coalesced to one single resonance (still flanked by ^{195}Pt satellites) upon raising the temperature. This dynamic NMR behavior can only be explained by rapid interchange between the in-plane and upright ethylene conformation, i.e., either rotation of the olefin around the platinum–ethylene bond axis or an oscillatory type of motion of the ethylene.

The observation of coupling of the platinum center with both the olefinic proton and carbon atoms in the whole temperature range studied excluded the occurrence of an alternative process involving rapid reversible platinum–olefin exchange (c.f. [PtCl$_2$(η^2-olefin)(R-dim)]^6).

The 100-MHz ^{1}H NMR spectra of the styrene complexes [PtCl$_2$(η^2-styrene)(6-R'-py-2-CH=NR)] were not easy to interpret because of the complexity resulting from the presence of two diastereomers in their various rotamer conformations. However, complete interpretation was achieved by recording the 250- and 360-MHz ^{1}H NMR spectra, two examples of which are shown in Figures 3 and 4 (see also Tables II and III). The ^{1}H NMR spectrum (25 °C, 360 MHz) of [PtCl$_2$-(η^2-styrene)(6-R'-py-2-CH=NR)], shown in Figure 3, reveals the presence of two isomeric species. This indicates that this complex exists in two rotameric forms as evidenced by the presence of two similar resonance patterns in an internal ratio of ca. 2:1. For example, the two singlets observed for the imine proton and the two singlets for the 6-Me protons appear in this approximate ratio as do the more complicated patterns of the spectrum, thus enabling a complete spectral assignment. Two prochiral groupings, labeled with a and b (a:b = 2:1 in

Table III. ^{13}C NMR Spectra of 6-R'-py-2-CH=NR and [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] Complexes

	T, °C	CH$_3$	CH$_2$	N–C	N=C	6-Mepy	C$_\alpha$=C$_\beta$
6-Hpy-2-CH=N-t-Bu	+34	28.91		56.79	155.64		
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Hpy-2-CH=N-t-Bu)]	+34	30.58		63.39	157.32		37.67 (305)
	−55	30.26		63.45	157.31		36.79 (302), 37.14 (302)
6-Mepy-2-CH=NC(H)Me$_2$	+34	23.47		60.81	159.02	23.68	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)Me$_2$)]	+34	23.93 (5)		63.19 (2 br)	160.50	26.65 (18)	34.85 (300), 35.50 (300)
6-Mepy-2-CH=NC(Me)$_2$Et	+34	8.60, 26.62	35.89	60.07	157.03	24.27	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(Me)$_2$Et)]^c	+34	8.76, 27.68	34.83	66.15 (21)	159.07	26.61 (18)	35.14 (300), 37.64 (300)
6-Mepy-2-CH=N-C(H)(Me)Ph^d	+34	23.87		69.08	160.39	24.17	
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=N-C(H)(Me)Ph)]^{b,d}	+34	20.79 (7)		67.85	161.83	27.68 (20)	36.80 (300)
	−55	21.60		67.44	161.50	26.96	35.63 (300), 36.27 (300)
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(Me)$_2$Et)]	−55	9.03, 25.99 26.80	33.98	66.23 (20)	160.83	26.43	32.77 (300), 50.82 (288)
		27.44 27.82	34.55		160.25	26.23	31.10 (307), 54.08 (294)
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(H)(Me)Ph)]^d	−55	19.54, 19.97^e		66.81,^{e} 67.56^e	161.16^e	26.52^e	30.55 (~300),^{e} 52.64 (~300),^{e} 31.30 (~300)^e
		21.09, 21.34^f		67.19,^{f} 68.17^f	160.21^f	27.34^f	31.80 (~300),^{f} 53.10 (~300),^{f} 31.92 (~300)^f

^{a} ^{13}C NMR spectra in CDCl$_3$; chemical shifts are relative to Me$_4$Si (ppm); $^nJ(^{195}$Pt–^{13}C) in parentheses are given in Hz. ^{b} Some decomposition during the measurement. ^{c} With very long pulsing time, $^nJ(^{195}$Pt–^{13}C) couplings were observed in the pyridyl ring: carbon resonances 125.43 (8), 128.14 (13), 138.90, 152.09 (7), and 161.00 (23). ^{d} The nitrogen C atom has the S configuration. ^{e} The complex exists in two diastereomeric forms in a 1:1 ratio, each diastereomer exist in two rotamers (2:1); the major is e. The minor rotamer is f.

Table IV. Infrared^{a,b} and Raman^c Spectra of [PtCl$_2$(py-2-CH=NR)] and [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)]

compds	ν(C=N)	ν_s(Pt–Cl)	ν_{as}(Pt–Cl)
cis-[PtCl$_2$(6-Hpy-2-CH=N-t-Bu)]^a	1626	319	346
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Hpy-2-CH=N-t-Bu)]^a	1644 (1642)	327 (326)	339 (339)
cis-[PtCl$_2$(6-Hpy-2-CH=N-C(H)(Me)Ph)]^{a,d}	1625	324	335
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Hpy-2-CH=NC(H)(Me)Ph)]^{a,d}	1649	326	334
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(Me)$_2$Et)]^b	1650 (1643)	(324)	330
[PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH=NC(H)(Me)Ph)]^{b,d}	1642 (1636)	317 (316)	333 (335)
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(Me)$_2$Et)]^b	1648 (1638)	(322)	332
[PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH=NC(H)(Me)Ph)]^{b,d}	1650		328

^{a} Infrared spectra recorded as Nujol mull between CsI plates. ^{b} IR recorded as KBr pellets. ^{c} Raman spectra recorded as pure compound are given in parentheses. ^{d} The nitrogen C atom has the S configuration.

Figure 3), are present in the C(CH$_3$)$_2$CH$_2$CH$_3$ substituent and are found to be diastereotopic since two singlets are observed both for the CH$_3$ protons and for the diastereotopic CH$_2$ protons (AB part of an ABM$_3$ pattern) due to coupling to the Me grouping. Likewise the 1:2 rotamer ratio enabled a first-order interpretation of both H$_{gem}$, H$_{trans}$, and H$_{cis}$ sets of the styrene ligand in the two rotamers. The ^{13}C NMR data (−55 °C for stability reasons) are consistent with the 360-MHz ^{1}H NMR results and likewise show separate resonance patterns for the two rotamers: four vinylic carbon resonances having different $^1J(^{195}$Pt–^{13}C) coupling were observed (see Table III).

When the prochiral C(CH$_3$)$_2$CH$_2$CH$_3$ imino substituent is replaced by a chiral (S)-C(H)(CH$_3$)Ph enantiomer, the five-coordinate complex exists in two diastereomeric forms. This is clearly reflected by the 250- and 360-MHz ^{1}H NMR spectra of [PtCl$_2$(η^2-styrene)(6-Mepy-2-CH=C(H)(Me)Ph)] shown in Figure 4 and Table II. Again each of the diastereomers is present in two rotameric conformations in an approximately 2:1 ratio denoted a and b, respectively. On the basis of ^{1}H–^{1}H double-resonance experiments, a complete assignment of the α-CH and α-CMe was possible (see Figure 4).

The ^{13}C NMR data given in Table III are consistent with the ^{1}H NMR results. A noteworthy phenomenon is the increased broadening (or even the absence) of the ^{195}Pt satellites when recording the ^{1}H NMR spectra of [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH=NR)] on subsequently the 60-, 100-, 250-, and 360-MHz NMR spectrometers. This is illustrated for the imine proton (CH=N), olefinic proton (=CH$_2$), and the

6-Me protons in Figure 5. Recently, this behavior has been explained in terms of ^{195}Pt/^{1}H chemical shift anisotropic relaxation.[12]

The 360-MHz ^{1}H NMR spectra clearly reveal the existence of the diastereomers in their rotameric forms but do not provide evidence about the olefin rotation process. From the observation of $J(^{195}$Pt–^{13}C) in the ^{13}C NMR spectra, it was concluded that the dynamic process did not involve a dissociation/association process of either the olefin or the L$_2$ ligand and thereby excludes the presence of an intermolecular process.

Discussion

The present complexes are the first examples of stable [PtCl$_2$(η^2-olefin)L$_2$] complexes in which the bidentate ligand system comprises two entirely different N-containing molecular halves. This enabled us to establish that in solution the ground-state structure comprises an array containing both the N—N and the C=C part of the olefin in the equatorial plane. This was not possible with the recently reported five-coordinate [PtX$_2$(η^2-olefin)L$_2$] (L$_2$ = α-diimine or diamine) complexes because of the symmetry in the equatorial plane.[6,9,10]

It has been shown that the stability of the platinum–olefin bond in five-coordinate complexes is strongly dependent on the σ-donating properties of the L$_2$ bidentate ligand trans to the olefin. This was explained on the basis of the Chatt–Dewar–Duncanson model. The σ donation by the L$_2$ ligand

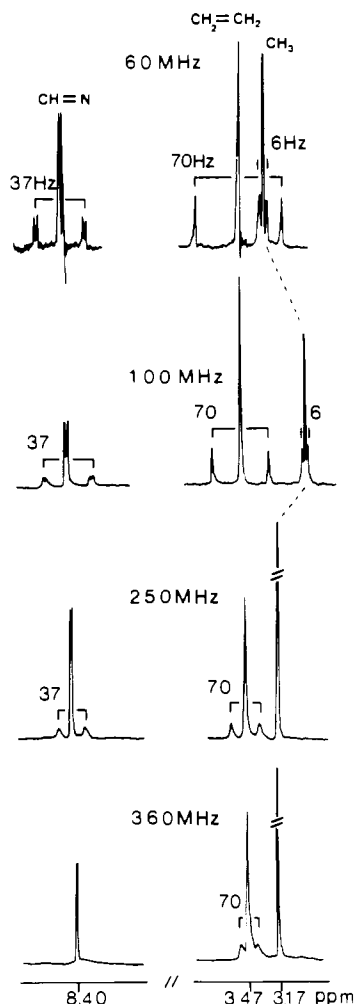(12) Lallemand, J. Y.; Soulié, J.; Chottard, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 436–438.

Figure 5. The imine proton (CH=N), olefinic protons (=CH₂), and 6-Me proton resonances of [PtCl₂(η²-C₂H₄)(6-Mepy-2-CH=N-(S)-CH(CH₃)(Ph))] observed on subsequently 60-, 100-, 250-, and 360-MHz spectrometers. The doublet of the imine proton, observable in all spectra, is due to a long-range $^4J(^1H-^1H)$ coupling (2 Hz) of (S)-CH (according to $^1H-^1H$ decoupling experiments).

causes an expansion of the platinum orbital (b₂) which is particularly suited for back-donation of electron density into the antibonding (π* 2p) orbital of the olefin. Increased σ donation therefore enhances the kinetic stability of the platinum–olefin bond.[6,13,14] The observed solution stability of the 6-R'-py-2-CH=NR complexes toward platinum–olefin bond dissociation according to eq 1 seems to be in accord with this view. The pyridine N atom in these types of ligands is a relatively weak electron donor whereas the imine N atom is relatively more electron releasing, particularly when alkyl groups like Me₃C or EtMe₂C are connected to it. Moreover the 6-Me-substituted compounds appeared to be far more stable than the unsubstituted compounds. At first, this seems in line with enhanced σ-donating properties of the pyridine N site as a result of the substitution. However, there is an additional effect, which is steric in nature and the influence of which on the overall solution stability is difficult to judge.

The 6-R'-py-2-CH=NR ligand completely resides in the equatorial plane of the trigonal-bipyramidal array. As a result the 6-Me substituent is also in this plane and therefore will represent considerable steric bulk, even greater than that of
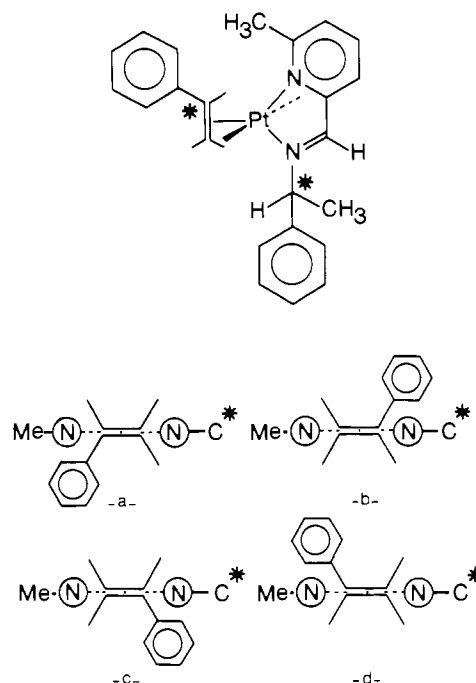
(13) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1953**, *18*, C79. (b) Chatt, M.; Duncanson, J. *J. Chem. Soc.* **1953**, 2939–2947.
(14) (a) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558–1565.

PtCl₂(styrene)(6-Me-Pyr-2-CH=N-Et Phenyl)

Figure 6. Ground-state structure of [PtCl₂(η²-styrene)(6-Mepy-2-CH=N-(S)-CH(CH₃)(Ph))]. Structures a–d are diastereomers. Structure a can be interconverted to b and c to d by a rotation of the styrene along the platinum–olefin bond.

the Me groups of a *t*-Bu substituent on the imine N because of the free rotation around the N–CMe₃ bond. The presence of potential steric bulk of the 6-Me group in the equatorial plane to one side of the Pt center probably has a large influence on the olefin dissociation decomposition of these complexes.

Whatever the actual route is for the decomposition of these five-coordinate complexes, in the resulting four coordinate *cis*-[PtCl₂(6-R'-py-2-CH=NR)] complexes the Pt–Cl bonds are coplanar with the Pt–N bonds. Comparison of the five-coordinate [PtCl₂(η²-olefin)(6-Mepy-2-CH=NR)] and the four-coordinate [PtCl₂(6-Mepy-2-CH=NR)] structures with each other shows that in particular in the square-planar structure the 6-Me group represents more steric hinderance with respect to the cis chlorine ligand than in the five-coordinate structure. Accordingly, introduction of the 6-Me group enhances the kinetic stability of the five-coordinate species with respect to the four-coordinate.

Interligand Chiral Recognition in the [PtCl₂(η²-styrene)(6-Mepy-2-CH=NR)] Complexes. Figure 6 shows that the equatorial plane of the five-coordinate [PtCl₂(η²-olefin)(6-Mepy-2-CH=NR)] complexes represents a molecular symmetry plane if the imino substituent R is achiral. Moreover when the coordinated olefin is of the type RR'C=CH₂ (R = R' ≠ H or R = H, R' ≠ H), this ground-state structure exists in two distinct conformations (rotamers) which are a result of the asymmetric pyridine–imine skeleton residing in the equatorial plane. These distinct conformations interconvert by rotation of the olefin around the platinum–olefin axis. (For review articles which discuss extensively the concept of the rotation about the platinum–olefin bonds, see ref 15 and 16.)

In the ¹H and ¹³C NMR spectra of all the styrene complexes which contain prochiral R substituents on the imino N atom, two rotamers are present in a 2:1 molar ratio. This indicates that not only interconversion by rotation of the styrene mol-

(15) Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799–844.
(16) Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* **1971**, *6*, 27–63.

ecule around the Pt–styrene bond axis is slow on the NMR time scale but that the isomers have different thermodynamic stability. Inspection of molecular models shows that the difference in stability probably arises from steric interaction in the equatorial plane since the axial ligands are identical (Cl). Possible interactions in the equatorial plane emerge from either the ═NR or the 6-Mepy[17] substituents. Since the different R groups (Me$_2$C(H) and EtMe$_2$C) similar molar ratios for the rotamers have been found, it seems plausible that the 6-Me is responsible for the observed rotameric discrimination rather than the constituents of the R group. These can adopt, by rotation around the C–N bond, the most favorable position with respect to the olefin, whereas the 6-Mepy group is held in the equatorial plane by the planarity of the py-2-CH═NR skeleton. Figure 2 illustrates the close proximites of the Me and the PhC═C skeleton. On the basis of these considerations, we assume that the more favorable rotamer has the phenyl group on the side of the imino R grouping (see Figure 6a–d). This view seems to be supported by the large $\Delta\delta$ of the diastereotopic Me groups[18] in ═N-i-Pr and ═NCMe$_2$Et (see Table II) resulting from shielding effects of the phenyl ring of the coordinated styrene molecule.

Interconversion of these rotamers (i.e., by olefin rotation) has not been observed. Note that in the case of the ethylene complexes olefin rotation could be established by NMR spectroscopy (vide supra).

The molecular symmetry present in the complexes with an achiral ═NR grouping is removed when R is a chiral grouping (e.g., [PtCl$_2$(η^2-styrene)(6-Mepy-2-CH═NR)] (R = (S)-CH(Me)(Ph)) (see Figure 6)). In this case we observed two different diastereomers each existing as a pair of rotamers. Also the interconversion of the rotamers by olefin rotation is then in the slow-rotation limit on the ^{1}H and ^{13}C NMR time scales and the 2:1 rotamer ratio for this compound indicates a similar difference in the thermodynamic stability. The observation that the complexes with the achiral Me$_2$C(H) and EtMe$_2$C and chiral PhMeC(H) grouping give a similar rotamer ratio is expected on the basis of the small steric differences.

The observation that the diastereomers of [PtCl$_2$(η^2-styrene)(6-Mepy-2-CH═N-(S)-CH(Me)(Ph))] exist in an almost 1:1 ratio indicates that chiral induction by the imino R group is very small. This might be due to the large separation between the chiral center and the prochiral olefin. It has recently been shown that even in the case where the chiral center is in the cis position in four-coordinate cis-[PtCl$_2$(η^2-olefin)(RR'SO)][19] the chiral induction was generally found to be small.

A distinct difference between the five-coordinate 6-R'-py-2-CH═NR compounds and the aforementioned four-coordinate complexes[19] is the observation that diastereomers of the 6-R'-py-2-CH═NR complexes do not undergo a second-order asymmetric transformation during crystallization.

The occurrence of fast epimerization catalyzed by non-coordinated styrene during the dissolution of the complexes, resulting in a 1:1 diastereomeric equilibrium, can be excluded because in separate experiments we found that olefin-exchange reactions do not occur with this class of compounds. This result

contrasts with the slow but selective olefin exchange exhibited by the related α-diimine and diamine complexes.[7,11] A possible reason for this inertness is the fact the the σN monodentate coordination of the py-2-CH═NR ligand, which would be a prerequisite for the exchange in these five coordinate Pt(II) species, is less accesible. In the σN coordination mode the ligand is necessarily only coordinated either to the pyridine N or the imino N atom in the s-trans conformation which is unfavorable because of steric interaction of the pyridyl H$_3$ and the imino H atom with ligands in the platinum coordination sphere.[20,21]

Conclusions

The [PtCl$_2$(η^2-olefin)(6-R'-py-2-CH═NR)] complexes are the first examples of five-coordinate platinum–olefin complexes in which the N coordination sites of the bidentate ligand are dissimilar. The resulting asymmetry in the equatorial plane of the trigonal-bipyramidal structure of these complexes could be used to establish by ^{13}C NMR that in solution and in the ground-state structure the olefinic C═C moiety resides in the equatorial plane. That this is the preferred olefin conformation was earlier anticipated on the basis of theoretical considerations and established in the solid by X-ray structure determinations, in particular for [PtCl$_2$(η^2-styrene)(t-Bu-dim)].[5,6] Changing the 6-R' substituent from H to Me appears to introduce a considerable increase of the steric constraints in the equatorial plane near the platinum center. This can explain the increased relative stability of the 6-Me complexes, with regard to platinum–olefin bond dissociation which affords square-planar cis-[PtCl$_2$(6-R'-py-2-CH═NR)] complexes. In the latter complexes all the ligands reside in one plane which necessarily brings one of the ligands (Cl) close to the 6-R substituent.

The degree of chiral recognition in the styrene complexes containing a chiral R substituent [(S)-C(H)(Me)Ph], with regards to selective coordination of one of the enantiomeric faces of the styrene, appears to be negligible probably due to the large distance between the coordination site and the chiral grouping. Moreover a 2:1 rotamer ratio was found in [PtCl$_2$(η^2-styrene)(6-Mepy-2-CH═NR)] (R = achiral or chiral substituent), reflecting the steric constraints introduced by the 6-Me group in the equatorial plane.

Registry No. PtCl$_2$(py-2-CH═N-t-Bu), 56171-64-3; PtCl$_2$(py-2-CH═NC(H)(Me)Ph), 78004-69-0; PtCl$_2$(η^2-C$_2$H$_4$)(py-2-CH═N-t-Bu), 78004-70-3; PtCl$_2$(η^2-C$_2$H$_4$)(py-2-CH═NC(H)(Me)Ph), 78004-71-4; PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH═NC(Me)$_2$Et), 78004-72-5; PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH═NC(H)(Me)Ph), 78004-73-6; PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH═NC(Me)$_2$Et), 78004-74-7; PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH═NC(H)(Me)Ph), isomer 1, 78004-75-8; PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH═NC(H)(Me)Ph), isomer 2, 78085-86-6; PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH═NC(H)Me$_2$), 78004-76-9; PtCl$_2$(η^2-C$_2$H$_4$)(6-Mepy-2-CH═NC(H)Ph$_2$), 78004-77-0; PtCl$_2$(η^2-C$_2$H$_3$Ph)(6-Mepy-2-CH═NC(H)Me$_2$), 78004-78-1; 6-Hpy-2-CH═N-t-Bu, 21478-42-2; 6-Hpy-2-CH═NC(H)(Me)Ph, 51705-23-8; 6-Mepy-2-CH═NC(H)Me$_2$, 78004-29-2; 6-Mepy-2-CH═NC(H)Ph$_2$, 78004-30-5; 6-Mepy-2-CH═NC(Me)$_2$Et, 78004-31-6; 6-Mepy-2-CH═NC(H)(Me)Ph, 78085-84-4; K-[PtCl$_3$(η^2-C$_2$H$_4$)], 12012-50-9; K[PtCl$_3$(η^2-C$_2$H$_3$Ph)], 12080-15-8.

(17) No conclusions could be drawn for the 6-R = H derivatives because they were not stable enough in solution to allow an extensive NMR study.
(18) That the Me and CH$_2$ parts of the prochiral iminosubstituents CMe$_2$Et and CMe$_2$H are diastereotopic in [PtCl$_2$(η^2-styrene)(6-R'-py-2-CH═NR)] exclude the presence of olefin as well as 6-R'-py-2-CH═NR dissociation–association mechanisms.
(19) Boucher, H.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6253–6261.

(20) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145–1151.
(21) van der Poel, H.; van Koten, G.; Vrieze, K.; Kokkes, M.; Stam, C. H. *Inorg. Chim. Acta* **1980**, *39*, 197–205.