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New cationic five-coordinate monoolefin hydrocarbyl complexes of platinum(II)

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Abstract

Cationic trigonal bipyramidal complexes of the type $[\text{PtRL}(\text{N}-\text{N}')(\text{olefin})]\text{BF}_4$ with various hydrocarbyl (R), neutral monodentate (L), and bidentate nitrogen ($\text{N}-\text{N}'$) ligands have been prepared and characterized by elemental analysis, conductivity measurements, and ^1H NMR spectroscopy. The coordination around Pt^{II} is trigonal bipyramidal, with the olefin and the $\text{N}-\text{N}'$ ligand in equatorial positions. The reversible loss of the olefin is markedly affected by the nature of the apical ligand L, which also influences stereochemical aspects, and by the steric requirements of $\text{N}-\text{N}'$.

Introduction

Since the first report [1] of a stable cationic five-coordinate Pt^{II} complex containing a $\text{C}=\text{C}$ bond in the ligand environment very few examples of cationic 18e^- monoolefin complexes of the nickel group elements have been described. Most of these are Pd^{II} and Pt^{II} species of the type $[\text{CpM}(\text{olefin})(\text{PPh}_3)]^+$ [2]. An ethylene tris(1-pyrazolyl)methane Pt^{II} complex has also been described [3]. A recent report [4] deals with five-coordinate ethylene neutral complexes $[\text{PtClMe}(\text{N}-\text{N}')(\text{C}_2\text{H}_4)]$, where $\text{N}-\text{N}'$ is a bidentate nitrogen ligand with appropriate steric requirements. A preliminary report of the first example of cationic five-coordinate monoolefin

complex of the type $[\text{PtRL}(\text{N}-\text{N}')(\text{olefin})]^+$, i.e. $[\text{PtMe}(\text{MeCN})(6\text{-Mepy-2-CH=NCMe}_3)(\text{C}_2\text{H}_4)]\text{BF}_4$, has also appeared [5].

At least three features prompted us to undertake further investigations on cationic complexes of the latter type namely: (i) the olefin coordination is reversible, and the influence of a wide choice of ligands on the corresponding free energy changes can be investigated; (ii) the availability of cationic and anionic [6] species, as well as the neutral ones mentioned above, provides a rare opportunity of comparing the stabilities and the reactivities [12*] of similar five-coordinate olefin hydrocarbyl d^8 complexes bearing different charges; (iii) cationic complexes bearing both a hydrocarbyl and an olefin ligand may possibly be related [7] to the recently discovered homogeneous catalysts for α -olefin polymerization based on group 4 metallocenes.

In continuation of our studies on five-coordinate olefin complexes of Pt^{II} and Pd^{II} , we report the synthesis and the spectroscopic characterization of a variety of cationic olefin hydrocarbyl complexes. Results concerning the equilibrium process of olefin release and stereochemical features of the new complexes are also discussed.

Experimental

^1H NMR spectra were recorded at 60 and 200 MHz on Varian T60 A and XL200 spectrometers, respectively. Conductivity measurements were made with an Orion Res. M.101 conductivity meter. Solvents and reagents were of Analar grade and were used without purification, except that for the synthesis of CF_3CN [8] the dichloromethane solvent was dried over P_2O_5 . Ligand **1** is the only $\text{N}-\text{N}'$ ligand commercially available as its monohydrate, which was dehydrated by a published procedure [9]. Ligands **2** [10], **3** [4] and **4** [4] were prepared by published methods. A previous report describes the synthesis of $[\text{PtClMe}(6\text{-Mepy-2-CH=NC}_6\text{H}_4\text{OMe})]$, [10]. Complexes of type $[\text{PtClMe}(\text{N}-\text{N}')(\text{olefin})]$ [4,10] and $[\text{PtClAr}(\text{N}-\text{N}')(\text{C}_2\text{H}_4)]$ [10] were also obtained by published procedures. The complexes were prepared and stored in air except for **3A'**, which was prepared under nitrogen. Analytical data for the cationic complexes are given in Table 1.

Synthesis of $[\text{PtR}(\text{MeCN})(\text{N}-\text{N}')(\text{olefin})]\text{BF}_4$ by halide abstraction. To a solution of $[\text{PtClR}(\text{N}-\text{N}')(\text{olefin})]$ (1.0 mmol) in 10 cm^3 of dichloromethane/MeCN (1/1) was added dropwise 4 cm^3 of 0.25 M AgBF_4 in the same solvent. After 10 min stirring the mixture was filtered through a thin layer of Celite. The filtrate was concentrated in vacuo to ca. 5 cm^3 . Addition of diethyl ether gave white crystals of the product. ^1H NMR data for the cationic complexes are listed in Table 2.

Synthesis of $[\text{PtRL}(\text{N}-\text{N}')(\text{olefin})]\text{BF}_4$ by ligand substitution. To a solution of $[\text{PtR}(\text{MeCN})(\text{N}-\text{N}')(\text{olefin})]\text{BF}_4$ (0.18 mmol) in dichloromethane (2 cm^3) was added an equimolar amount of ligand L. The solution was stirred 3 h at room temperature. Filtration followed by removal of the solvent in vacuo afforded the crude product. This was dissolved in a minimum amount of dichloromethane and diethyl ether was added to give the product as white crystals ($\text{N}-\text{N}' = 2,9\text{-Me}_2\text{-1,10}$ -phenanthroline) or pale yellow glassy solids.

* Reference number with asterisk indicates a note in the list of references.

Table 1

Elemental analysis for [PtRL(N-N')(olefin)]BF₄ complexes (calculated values in parentheses (%))

Compound	mol. formula	C	H	N
1A'a	C ₁₉ H ₂₂ BF ₄ N ₃ Pt	39.75 (39.75)	3.75 (3.85)	7.25 (7.30)
1A'b	C ₂₂ H ₂₈ BF ₄ N ₃ Pt	42.70 (42.85)	4.55 (4.60)	6.55 (6.80)
1A'c	C ₁₉ H ₂₅ BF ₄ N ₂ PtS	38.30 (38.35)	4.15 (4.25)	4.65 (4.70)
1A'd	C ₁₈ H ₂₄ BF ₄ N ₃ Pt	38.30 (38.30)	4.25 (4.30)	7.50 (7.45)
1A'e	C ₂₂ H ₂₄ BF ₄ N ₃ Pt	43.10 (43.15)	3.95 (3.95)	7.00 (6.85)
1A'f	C ₂₃ H ₂₆ BF ₄ N ₃ Pt	44.05 (44.10)	4.10 (4.20)	6.80 (6.70)
1A''a	C ₂₀ H ₂₄ BF ₄ N ₃ Pt	40.95 (40.85)	4.10 (4.10)	7.20 (7.15)
2A'a	C ₁₉ H ₂₄ BF ₄ N ₃ OPt	38.45 (38.55)	4.10 (4.10)	7.15 (7.10)
2A'b	C ₂₂ H ₃₀ BF ₄ N ₃ OPt	41.50 (41.65)	4.60 (4.80)	6.45 (6.60)
2A'g	C ₁₉ H ₂₁ BF ₇ N ₃ OPt	35.15 (36.30)	3.45 (3.30)	6.25 (6.50)
2B'a	C ₂₅ H ₂₈ BF ₄ N ₃ O ₂ Pt	44.00 (43.90)	4.20 (4.10)	6.15 (6.15)
2C'a	C ₂₅ H ₂₅ BF ₇ N ₃ OPt	41.50 (41.60)	3.40 (3.50)	5.75 (5.80)
3A'a	C ₁₆ H ₂₆ BF ₄ N ₃ Pt	35.40 (35.45)	4.70 (4.85)	7.80 (7.75)
4A'a	C ₂₀ H ₂₆ BF ₄ N ₃ Pt	40.75 (40.70)	4.50 (4.45)	7.05 (7.10)
4A'h	C ₂₅ H ₃₂ BF ₄ N ₃ Pt	45.85 (45.75)	5.05 (4.90)	6.50 (6.40)

Synthesis of [PtMe(CF₃CN)(6-Mepy-2-CH=NC₆H₄OMe)(C₂H₄)]BF₄. To a solution of [PtClMe(6-Mepy-2-CH=NC₆H₄OMe)(C₂H₄)] (0.250 g, 0.5 mmol) in dichloromethane was added a solution of AgBF₄ (0.097 g, 0.5 mmol) in dichloromethane (2 cm³) containing enough tetrahydrofuran to ensure dissolution of the salt. The mixture was stirred for 0.5 h and filtered. The filtrate was collected in a Schlenk tube, then cooled at -60 °C as a slow stream of CF₃CN was bubbled through for 2 h. The solution was reduced in volume and diethyl ether was added until a cloudiness developed. The mixture was filtered through a thin Celite layer and hexane was added to the filtrate to precipitate the product as a yellow oil, which was transformed into a glassy solid upon standing in vacuo.

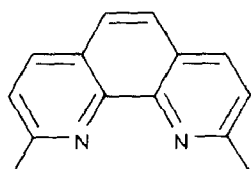
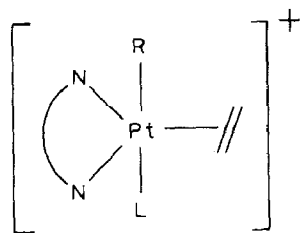
Synthesis of [PtMe(MeCN)(6-Mepy-2-CH=NC₆H₄OMe)(C₂H₄)]BF₄ by ethylene uptake. The parent complex [PtMe(MeCN)(6-Mepy-2-CH=NC₆H₄OMe)]BF₄ was obtained from [PtClMe(6-Mepy-2-CH=NC₆H₄OMe)] under conditions similar to those described above for halide abstraction from five-coordinate species (Found: C, 53.80; H, 3.53; N, 7.29. C₁₇H₂₀BF₄N₃OPt calcd.: C, 53.93; H, 3.55; N, 7.39%); ¹H NMR (CDCl₃/CD₃NO₂ 4/1): δ 9.0 (s, 1 H, ³J(PtH) 95 Hz), 8.1–6.8 (m, 7 H,

Table 2
Selected ^1H NMR data for $[\text{PtR}(\text{L})(\text{N}-\text{N}')(\text{olefin})]^+$ complexes (as fluoroborate salts) ^a

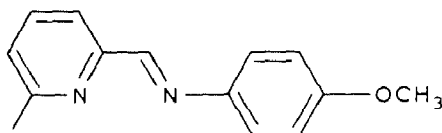
No.	Complex	Pt-Me	N-CMe (heteroaromatic)	$\times\text{C}=\text{C}\times$	Other
1A'a	$[\text{PtMe}(\text{MeCN})(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	-0.01(71)	3.30(6)	2.21(6s,d,2H), 2.88(80,d,2H)	1.95(4,MeCN)
1A'b	$[\text{PtMe}(\text{Me}_3\text{CCN})(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	0.05(70)	3.26(6)	2.35(6s,d,2H), 2.80(80,d,2H)	1.13(Me ₃ C)
1A'c	$[\text{PtMe}(\text{Me}_2\text{S})(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	0.20(62)	3.25(6)	2.35(67,d,2H), 2.65(80,d,2H)	1.88(14,Me ₂ S)
1A'd	$[\text{PtMe}(\text{MeNH}_2)(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	-0.15(63)	3.27(6)	2.30(67,d,2H), 2.54(80,d,2H)	1.85(13,t,MeN), 2.34(m,NH ₂)
1A'e	$[\text{PtMe}(\text{pyridine})(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	0.22(65)	3.46(6)	2.51(75,4H)	4.47(NH ₂)
1A'f	$[\text{PtMe}(\text{PhNH}_2)(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{C}_2\text{H}_4)]^+$	0.06(68)	3.14(6)	2.29(68,d,2H), 2.72(84,d,2H)	2.00(4,MeCN), 1.49(56,d,Me)
1A''a	$[\text{PtMe}(\text{MeCN})(2,9\text{-Me}_2\text{-1,10-phenanthroline})(\text{MeCH}=\text{CH}_2)]^+$	-0.03(71)	3.25(6) 3.31(6)	2.42(76,m,1H), 2.9(m,2H)	1.94(MeCN), 3.81(OMe), 9.39(38,N=CH)
2A'a	$[\text{PtMe}(\text{MeCN})(6\text{-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})(\text{C}_2\text{H}_4)]^+$	0.01(71)	2.94(5)	2.20(67,m,2H), 2.78(84,m,2H)	1.20(Me ₃ C), 3.83(OMe), 9.47(39,N=CH)
2A'b	$[\text{PtMe}(\text{Me}_3\text{CCN})(6\text{-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})(\text{C}_2\text{H}_4)]^+$	0.12(72)	3.04(5)	2.3(m,2H), ^c 2.76(m,2H) ^c	3.84(OMe), 9.22(42,N=CH)
2A'g	$[\text{PtMe}(\text{CF}_3\text{CN})(6\text{-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})(\text{C}_2\text{H}_4)]^+$	0.22(74,br)	2.9(br)	2.0-3.0(4H,br)	1.28(55,d,MeC=), 9.35(40,N=CH)
2A''a	$[\text{PtMe}(\text{MeCN})(6\text{-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})(\text{MeCH}=\text{CH}_2)]^+$	0.02(72)	2.93(5)	2.27(80,d,1H), 2.65(80,d,1H)	1.35(60,d,MeC=), 9.34(33,N=CH)
2A'''f	As above, diastereomer, ^d 40% abundance $[\text{PtMe}(\text{PhNH}_2)(6\text{-Mepy-2-CH}=\text{NC}_6\text{H}_4\text{OMe})\text{-}(\text{MeOCOCH}=\text{CH}_2)]^+$	0.00(72) 0.34(66)	2.99(5) 2.58(5)	2.23(80,d,1H), 2.63(80,d,1H) 5.1(m,OC-CH=), ^e 3.27(75,d,1H), 3.1(d,1H)	9.32(38,N=CH)

	As above, diastereomer, ^{e,f} 40% abundance	0.32(67)	2.58(5)	5.0(m,OC-CH=), ^c 3.32(75,d,1H) 3.0(d,1H)	9.22(38,N=CH)
2B'a	[Pt(4-MeO-C ₆ H ₄)(MeCN)- (6-Mepy-2-CH=NC ₆ H ₄ OMe)(C ₂ H ₄)] ⁺		3.30(5)	2.50(m,2H) ^c 3.18(m,2H) ^c	2.26(5,MeCN), 3.85(OMe), 3.60(OMe), 9.22(40,N=CH) 2.27(5,MeCN), 3.94(OMe), 9.21(40,N=CH)
2C'a	[Pt(4-CF ₃ -C ₆ H ₄)(MeCN)- (6-Mepy-2-CH=NC ₆ H ₄ OMe)(C ₂ H ₄)] ⁺ ^f		3.32(5)	2.5(67,m,2H), 3.23(86,m,2H)	1.52(CMe ₃), 2.09(5,MeCN), 9.12(41,N=CH)
3A'a	[PtMe(MeCN)(6-Mepy-2-CH=N-t-Bu)(C ₂ H ₄)] ⁺	-0.07(71)	2.91(5)	2.06(67,d,2H), 2.69(83,d,2H)	1.71(MeCN), 1.88(d,CHMe), 9.29(42,N=CH)
4A'a	[PtMe(MeCN)(6-Mepy-2-CH=N-(S)-CH(Me)Ph)(C ₂ H ₄)] ⁺	-0.01(71)	2.88	2.0-2.8(m) ^g	2.08(MeCN), 1.97(d,CHMe), 9.25(42,N=CH)
	As above, diastereomer 40% abundance		2.88	2.0-2.8(m) ^g	1.92(d,CHMe), 2.16(CMe), 3.42(m,NH ₂), 9.48(40,N=CH)
4A'h	[PtMe(4-MeC ₆ H ₄ NH ₂) (6-Mepy-2-CH=N-(S)-CH(Me)Ph)(C ₂ H ₄)] ⁺	-0.04(69)	2.62(5)	1.8-2.5(m) ^g	2.00(d,CHMe), 2.20(CMe), 3.42(m,NH ₂) ^f , 9.20(40,N=CH)
	As above, diastereomer 30% abundance		2.57(5)	1.8-2.5(m) ^g	

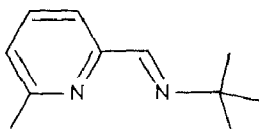
^a 200 or 270 MHz, CDCl₃. Abbreviations: d, doublet; m, multiplet; br, broad peak; no attribute = singlet. Fine structure due to long-range coupling ($J < 2$ Hz) is ignored. Coupling constants to ¹⁹⁵Pt are given in parentheses. ^b Spectrum recorded at 60 MHz. ^c ¹⁹⁵Pt satellite peaks too weak and/or broad to be detected. ^d Only two of the four possible diastereomers were detectable. ^e Two minor diastereomers were also detectable. ^f 10% of CD₃NO₂ added to improve solubility. ^g Partly or totally overlapped by other signals.



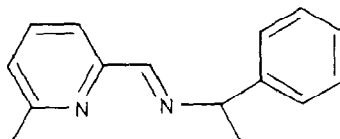
1



2



3



4

Scheme 1. **a**: L = CH₃CN, **b**: L = (CH₃)₃CCN, **c**: L = (CH₃)₂S, **d**: L = CH₃NH₂, **e**: L = C₅H₅N, **f**: L = C₆H₅NH₂, **g**: L = CF₃CN, **h**: L = 4-CH₃C₆H₄NH₂; **A**: R = CH₃; **B**: R = 4-CH₃O-C₆H₄; **C**: R = 4-CF₃-C₆H₄.

arom.), 3.77 (s, 3 H, MeO), 2.77 (s, 3 H, 6-Me), 1.95 (s, 3 H, MeCN, ⁴J(PtH) 16 Hz), 0.72 (s, 3 H, Me-Pt, ²J(PtH) 78 Hz).

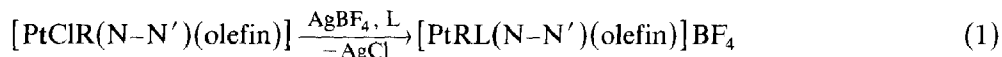
A solution of [PtMe(MeCN)(6-Mepy-2-CH=NC₆H₄OMe)]BF₄ in a minimum of dichloromethane was stirred for 5 h under ethylene (ca. 2 atm). Addition of diethyl ether gave crystals of the product.

Results and discussion

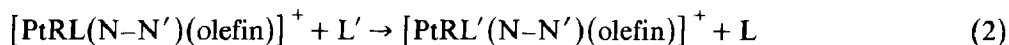
Synthesis and characterization

The complexes are listed in Table 2, where the relevant ¹H NMR data are given, together with the notations used for the labelling of the compounds. The number refers to the bidentate ligand N-N', the capital letter to the hydrocarbyl groups R, the primes to the olefin ligand (', ethylene; '', propylene; ''', methyl acrylate) and the small letter to the neutral ligand L.

Neutral complexes were prepared as reported previously [4,10], and used as starting materials for the synthesis of the cationic species (eq. 1). This involves abstraction of one halide ligand and coordination of the neutral ligand L.



An alternative method (eq. 2) for the synthesis of some of the complexes involved



the replacement by a different ligand L of methyl cyanide in a complex previously prepared according to eq. 1. We made species with L = MeCN, CF₃CN, and Me₃CCN by the first procedure and those with L = pyridine, PhNH₂, MeNH₂ and Me₂S by the exchange method. Both the methyl cyanide and the ethylene ligands were removed when 1,5-cyclooctadiene was used in the displacement procedure. In this case the five-coordinate complex [PtMe(2,9-Me₂-1,10-phenanthroline)(1,5-cyclooctadiene)]BF₄ was formed.

The cationic complexes were obtained as white crystalline solids for N-N' = 1. With the other chelate ligands the complexes were usually recovered as pale yellow to yellow glassy materials by removing the solvent from dichloromethane solution. The solubility in dichloromethane or chloroform is usually poor, while moderate for the methyl cyanide derivatives. All the complexes are soluble in nitromethane. Conductivities were consistent with the complexes' being 1/1 electrolytes.

The more relevant ¹H NMR resonances are reported in Table 2. The five-coordinate bipyramidal structure * was assigned to the complexes on the basis of the signal multiplicities and the chemical shifts of the olefinic protons. A detailed discussion of how the bipyramidal structure can be unambiguously established from ¹H NMR data for [PtClMe(N-N')(C₂H₄)] complexes has been presented before [4], and similar arguments are valid in the case of the cationic species, in which the chloride ion has been replaced by a neutral ligand in an axial position.

In the cationic complexes there is restricted rotation around the metal-olefin bond. In the case of unsymmetrical N-N' ligands the ethylene resonances (Table 2) appear as complex multiplets, while in the case of the symmetrical ligand 1 they appear as two pseudo-doublets (flanked by ¹⁹⁵Pt satellite peaks) which actually consist of an AA'-XX' multiplet. In contrast with the behaviour of four-coordinate cationic Pt-olefin complexes [11], the positive charge does not cause any appreciable down-field shift of the signal for olefinic protons, compared with that for the corresponding neutral species [4,10]; in fact there is an upfield shift in the range 0.2-0.4 ppm in most cases for the downfield component of the olefinic multiplet.

Stability of the complexes

Previous studies [4,10] in neutral complexes provided evidence for an equilibrium involving a four-coordinate species [PtClR(N-N')] and the free olefin. This meant that we could investigate the influence of the coordination environment on the stability of the five-coordinate species [10]. In complexes with the same olefin, the dominant factor was found to be the steric hindrance on both sides of the N-N' ligand. If appropriately oriented in the coordination plane this stabilizes the bipyramidal complex through a corresponding destabilization of the square-planar species [9]. In complexes of a given N-N' ligand, the dominant stabilizing factor

* Preliminary results from the X-ray diffraction study of the crystal structure of (2,9-dimethylphenanthroline)(ethylene)(methyl)(methyl cyanide)platinum(II) tetrafluoroborate unequivocally confirmed the TBP geometry and the proposed stereochemistry of the cation. However, probably owing to disorder in the anion packing, the molecular structure resolution was unsatisfactory. Further X-ray diffraction studies are in progress on other salts of the cation.

Table 3

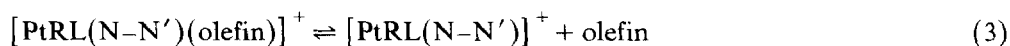
Olefin dissociation pK 's (T 33°C) for some $[\text{PtRL}(6\text{-Mepy-2-CH=NC}_6\text{H}_4\text{OMe})(\text{olefin})]^+$ complexes and the corresponding chloride species

Apical ligand	Olefin	
	Propylene	Methyl acrylate
Cl^-	1.4 ^a	3.0 ^a
MeCN	0.9	1.7
pyridine	-0.6	0.5
aniline	1.6	> 3

^a From ref. 10.

was found to be the electron-withdrawing ability of the substituents on the olefinic bond, demonstrating the importance of π -back-donation in the five-coordinate species.

We have observed the same type of equilibrium (eq. 3) in solutions of the cationic



compounds, and the same trend in respect of the effect of the ligands on the dissociation equilibrium. Thus the most stable complexes are those with $\text{N}-\text{N}' = \mathbf{1}$ [4,10], which do not lose the olefin even in boiling chloroform, and the complexes with methyl acrylate are more stable than those with propylene. We note that olefin uptake by a $16 e^-$ cation, according to equation 3, can be used in a preparative method for obtaining a five-coordinate species. In fact, in a preliminary stage of a study of $[\text{PtRL}(\text{N}-\text{N}')]^+$ complexes we have prepared $\mathbf{3A}'\mathbf{a}$ by ethylene addition to $[\text{PtMe}(\text{MeCN})(6\text{-Mepy-2-CH=NC}_6\text{H}_4\text{OMe})]\text{BF}_4$.

In order to investigate the effect of the positive charge and of the axial ligand L on the stability of the new cationic species, we have determined the dissociation pK 's of some propylene and methyl acrylate complexes by the ^1H NMR procedure previously used for the neutral species [4,10]. The values are reported in Table 3, together with those for the corresponding chloride complexes [10], for comparison. It can be seen that the stability of the five-coordinate species is markedly affected by the ligand L, and variations of more than two orders of magnitude are observed. If the neutral chloride complexes are used as a reference, the cationic species appear to be, on the average, less stable, as found for the four-coordinate Pt-olefin complexes. However, the destabilizing effect of the positive charge does not seem to be dominant, since the electronic and steric features of the individual L ligands can overcome it, as demonstrated by the high stability of the aniline complexes. While the effects of equatorial ligands on the olefin dissociation equilibrium can be easily understood, being essentially the same in the neutral and the cationic species, it does not seem possible at this stage to rationalize fully the influence of the axial L ligands. However totally empirical this influence can be used to modulate the stability of a complex containing given olefinic and $\text{N}-\text{N}'$ ligands.

Stereochemical features

In complexes with TBP geometry of the type here discussed, bearing two different apical ligands, non-equivalence of the two halves of the chelate ligand ($\text{N}-\text{N}'$) makes the metal atom a stereogenic center. In case of neutral complexes the

chirality was resolved [4] by the use of a chiral imine, through the isolation of the pure diastereoisomer C -[PtClMe{6-Mepy-2-CH=N-(*S*)-CH(Me)Ph}(C₂H₄)], whose absolute configuration was determined by X-ray crystallography [4]. The equilibrium ratio of the two diastereomers of this compound was found to be about 5/3 in chloroform solution. The corresponding cationic complexes **4A'a** and **4A'h**, having methyl cyanide and *p*-toluidine as axial ligands also given diastereomeric pairs at equilibrium, in about 3/5 and 3/7 ratio, respectively, as can be seen from their ¹H NMR spectra (Table 2). In an attempt to correlate the stereochemistries of the two cationic species with those of their parent chloride complexes, the axial ligands were displaced with a slight excess of chloride ions and the reaction was monitored by ¹H NMR spectroscopy. In both cases, immediately following the fast displacement reaction, a mixture of the two diastereomeric chloride complexes was present, containing the less stable isomer as the major product. The mixture subsequently undergoes epimerization to reach the expected final equilibrium composition. The absolute configuration of the most abundant diastereomer in the two cationic species thus appears to be the opposite of that in the corresponding neutral chloride complexes. The above results can also be explained in terms of the preferential formation of the less stable diastereomer by kinetically controlled addition of chloride to an intermediate not containing a stereogenic metal centre. In both cases, it appears that the stereochemical properties of the complexes can be considerably affected by appropriate choice of axial ligands. As an example we note that the two expected isomers (rotamers around the Pt-olefin bond) were previously observed [10] for the chloride propylene complex [PtClMe(2,9-Me₂-1,10-phenanthroline)(CH₂=CHMe)] in an equilibrium ratio of 65/35. The same isomers are observed for the cationic complex [PtMe(MeCN)(2,9-Me₂-1,10-phenanthroline)(CH₂=CHMe)] in a ratio of 95/5.

Conclusions

Our results show that a moderately wide variation of the axial ligand can be fairly readily achieved within the class of the cationic trigonal bipyramidal complexes [PtRL(N-N')(olefin)]⁺. The variation of the L ligand can be used to modulate the stability of the complexes with respect to the olefin dissociation reaction and to induce stereochemical effects on the chiral metal center and on the olefin coordination. Further studies on the reactivity of the cationic species and the stereochemistry of olefin coordination are in progress.

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