Organometallics 1987, *6*, 517–525

Five-Coordinate Olefin Complexes of Platinum(II) Containing σ-Bonded Carbon Ligands. Synthesis and Characterization of [PtClMe(η^2-C$_2$H$_4$)(N-N′)] Complexes. Molecular Structure of an Adduct with a Chiral Metal Center and of Its Parent Four-Coordinate Complex

Vincenzo G. Albano and Dario Braga

Istituto Chimico G.Ciamician, Università di Bologna, 40126 Bologna, Italy

Vincenzo De Felice, Achille Panunzi, and Aldo Vitagliano*

Dipartimento di Chimica, Università di Napoli, 80134 Napoli, Italy

Received July 14, 1986

Addition of the bidentate ligands Me$_2$NN=C(Me)C(Me)=NNMe$_2$, *t*-BuN=CHCH=N-*t*-Bu, Me$_2$N—CH$_2$CH$_2$—NMe$_2$, *i*-PrNH—CH$_2$CH$_2$—NH-*i*-Pr, and 6-Rpy-2-CH=NR′ (R = H, Me; R′ = Me, CH$_2$Ph, (*S*)-CH(Me)Ph, *t*-Bu) to [PtClMe(η^2-C$_2$H$_4$)]$_2$ gives the five-coordinate complexes [PtClMe(η^2-C$_2$H$_4$)(N-N)]. These can lose ethylene reversibly, giving the corresponding four-coordinate complexes [PtClMe(N-N)], in an equilibrium that appears to be controlled by the steric bulk of the nitrogen substituents. The five-coordinate complexes can also be prepared by ligand displacement from the cyclooctadiene complex [PtClMe(COD)] with the appropriate N-N ligand and successive (or simultaneous) uptake of ethylene. In the case of unsymmetrical imines 6-Rpy-2-CH=NR′ the five-coordinate complexes contain a chiral platinum atom. This was resolved by the use of the chiral imine 6-Mepy-2-CH=N-(*S*)-CH(Me)Ph (**9**), which after crystallization gave the pure diastereomer *C*-[PtClMe(η^2-C$_2$H$_4$)(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)] (**9a′**). The crystal structures of **9a′** and of its parent four-coordinate complex [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)] (**9b**) have been determined by X-ray diffraction. **9b** crystallizes in the orthorombic system, space group $P2_12_12_1$, with a = 9.354 (1) Å, b = 10.555 (2) Å, c = 16.290 (1) Å, and Z = 4. **9a′** crystallizes in the monoclinic system, space group $P2_1$, with a = 8.524 (1) Å, b = 10.921 (2) Å, c = 10.017 (1) Å, β = 105.20 (1)°, and Z = 2. Refinements converged at R = 0.021 for **9b** and R = 0.020 for **9a′**. The bond parameters of the trigonal-bipyramidal **9a′** are in agreement with a quite relevant platinum–ethylene π-back-bonding (Pt—C = 2.053 (6) Å and C=C = 1.415 (11) Å). The geometric features of **9b** support the idea that the stabilization of a trigonal-bipyramidal complex by the N-N′ ligand can be attributed to a destabilization of the corresponding square-planar complex by repulsive interactions of the side groups of the N-N′ ligand with the Me and Cl ligands.

Introduction

Stable five-coordinate complexes of platinum(II) were almost unknown until about 1973.[1] During the following years a number of chelating nitrogen ligands, when combined with a π-acceptor ligand like an olefin or an acetylene, were found to stabilize the five-coordination for the Pt(II) ion.[2-10] Nearly all the compounds of this type so far described belong to two classes: (i) [PtMe(η^2-olefin)(N$_3$)], where N$_3$ is the tridentate anionic ligand hydrotris(1-pyrazolyl)borate,[2] and (ii) [PtCl$_2$(η^2-olefin)(N-N)], where N-N is a neutral bidentate nitrogen ligand such as a diamine,[3,4] a bis(hydrazone),[5,7] or a diimine.[4b,7-10] The wide number of N-N ligands giving class ii compounds allowed their steric and electronic properties to be correlated with the stability of the five-coordinate species. The stability was found to be increased by the π-acceptor ability of the olefin.[7] It was also markedly affected by the steric requirements of the chelating ligand[3,4,7,8,10] and to some extent by its donor properties.[6-9] However, as far as the dissociation of the olefin is involved in the loss of the five-coordination, the term "stability", widely used in the literature, has to be regarded in a kinetic rather than in a thermodynamic sense, since there are no reports that the dissociation of the olefin from type ii complexes is reversible. The only observed equilibrium between the four- and five-coordinate states involved the dissociation of one terminus of the bidentate ligand.[4,7,9] On the other hand, the preparation of class i complexes consisted in a direct uptake of the olefin by a four-coordinate polymeric species,[2] and likewise the methyl complex [PtClMe(bipyridyl)][11] has been reported to give adducts with strongly electron-withdrawing olefins and acetylenes.[12] These results, compared with those obtained for class ii compounds, show that the presence on the metal of the powerful methyl donor probably stabilizes the metal–olefin bond in a five-coordinate complex, or at least it activates the four-coordinate complex toward the olefin addition. As an extension of previous work from our laboratory on five-coordination in Pt(II) chemistry,[3,7,13] we were

---

[1] Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, 1974; pp 35–40. Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; pp 146–149.

[2] (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1996. (b) Manzer, L. E. *Ibid.* **1976**, *15*, 2354.

[3] (a) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549. (b) De Renzi, A.; Di Blasio, B.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Chem.* **1980**, *19*, 960.

[4] (a) Maresca, L.; Natile, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1140. (b) van der Poel, H.; van Koten, G.; van Stein, G. C. *J. Chem. Soc., Dalton Trans.* **1981**, 2164.

[5] Cattalini, L.; Gasparrini, F.; Maresca, L.; Natile, G. *J. Chem. Soc., Chem. Commun.* **1973**, 369.

[6] Maresca, L.; Natile, G.; Calligaris, M.; Delise, P.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2386.

[7] Albano, V. G.; Demartin, F.; De Renzi, A.; Morelli, G.; Saporito, A. *Inorg. Chem.* **1985**, *24*, 2032.

[8] Maresca, L.; Natile, G.; Cattalini, L. *Inorg. Chim. Acta* **1975**, *14*, 79.

[9] van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941.

[10] van der Poel, H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2950.

[11] Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

[12] Chaudhury, N.; Kekre, M. G.; Puddephatt, R. J. *J. Organomet. Chem.* **1974**, *73*, C17. Chaudhury, N.; Puddephatt, R. J. *Ibid.* **1975**, *84*, 105. Chaudhury, N.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 467.

0276-7333/87/2306-0517$01.50/0

Table I. Selected ^{1}H NMR Data (δ) for [PtClMe(η^2-C_2H_4)(N-N)] and [PtClMe(N-N)] complexes[a]

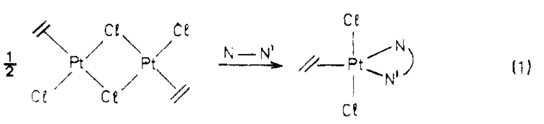
no.	complex	Pt-*Me*	N=*CH* or N=C*Me*	N-$CH_x(R)_{3-x}$	6-H or 6-*Me*	$CH_2=CH_2$
1a	[PtClMe(C_2H_4)($Me_2NN=C(Me)C(Me)=NNMe_2$)]	0.05 (71)	2.42 (4)	2.94		2.07 (64, d),[b] 2.87 (83, d)[b]
2a	[PtClMe(C_2H_4)(*t*-Bu-N=CHCH=N-*t*-Bu)]	−0.05 (70)	8.73 (34)			2.50 (~70, br)
3a	[PtClMe(C_2H_4)(Me_2N—CH_2CH_2—NMe_2)][c]	0.26 (65)		2.53 (13), 2.77 (25)		2.4 (~80 m)
4a	[PtClMe(C_2H_4)(Me_2CHNH—CH_2CH_2—$NHCHMe_2$)][c]	0.03 (70)		3.5 (m),[d,e]- 3.0 (m)[d,e]		1.71 (t),[d] 1.82 (63, t), 2.47 (t),[d] 2.65 (t)[d,e]
5a	[PtClMe(C_2H_4)(6-Hpy-2-CH=NMe)][c]	−0.10 (70)	8.93 (39)	4.05 (18)		2.80 (80, 2 H, m), 2.13 (65, t), 2.00 (60, t)
6a	[PtClMe(C_2H_4)(6-Hpy-2-CH=N-*t*-Bu)]	−0.03 (72)	8.91 (37)		9.11 (18, d)	2.85 (84, 2 H, m), 2.11 (60, t), 2.02 (60, t)[e]
7a	[PtClMe(C_2H_4)(6-Mepy-2-CH=NMe)]	−0.06 (72)	8.86 (40)[f]	4.06 (22)[f]	3.06 (5)	2.80 (82, d), 2.06 (63, d)[e,g]
8a	[PtClMe(C_2H_4)(6-Mepy-2-CH=NCH_2Ph)]	−0.38 (70)	8.77 (38)[f]	5.48 (1 H, d)[f] 5.27 (1 H, d)[h]	3.04 (5)	2.81 (84, 2 H, m), 1.93 (60, t), 1.81 (65, t)[e]
9a′	*C*-[PtClMe(C_2H_4)(6-Mepy-2-CH=N-(*S*)-CH-(Me)Ph)]	−0.40 (71)	8.73 (37)[f]	5.35 (q)[f]	3.04 (5)	2.99 (~80, t), 2.89 (~80, t), 2.01 (~60, 2 H, m)[e]
9a″	*A*-[PtClMe(C_2H_4)(6-Mepy-2-CH=N-(*S*)-CH-(Me)Ph)]	−0.18 (71)	8.56 (38)[f]	5.49 (q)[f]	3.06 (5)	*i*
10a	[PtClMe(C_2H_4)(6-Mepy-2-CH=N-*t*-Bu)]	−0.05 (70)	8.90 (37)		3.08 (5)	2.94 (80, br), 2.15 (65, br)
1b	[PtClMe($Me_2NN=C(Me)C(Me)=NNMe_2$)]	1.51 (78)	2.10 (4) 1.85 (13)	3.12, 2.91		
3b	[PtClMe(Me_2N—CH_2CH_2—NMe_2)]	0.60 (78)		2.80 (53, 2.67 (13)		
5b$_c$	[PtClMe(6-Hpy-2-CH=NMe)]	1.33 (78)	9.06 (102)[f]	4.03 (47)[f]	9.44 (13, d)	
5b$_t$	[PtMeCl(6-Hpy-2-CH=NMe)]	1.32 (78)	8.80 (38)[f]	4.00 (13)[f]	9.18 (58, d)	
6b	[PtMeCl(6-Hpy-2-CH=N-*t*-Bu)]	1.55 (81)	8.68 (37)		9.21 (59, d)	
7b	[PtClMe(6-Mepy-2-CH=NMe)]	1.45 (82)	9.10 (100)[f]	3.93 (48)[f]	3.16	
8b	[PtClMe(6-Mepy-2-CH=NCH_2Ph)]	1.43 (84)	8.93 (100)[f]	5.28 (42)[f]	3.16	
9b	[PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)]	1.48 (82)	8.86 (100)[f]	5.79 (37, q)[f]	3.15	

[a] 270 MHz, $CDCl_3$. Abbreviations: d = doublet; t = triplet; q = quartet; m = multiplet; br = broad peak; no attribute = singlet. Coupling constants (Hz) to ^{195}Pt are given in parentheses. [b] Pseudodoublets, actually constituting a AA′XX′ multiplet. [c] Spectrum recorded at −30 °C to avoid dissociation and/or freeze dynamic behavior. [d] The ^{195}Pt satellite peaks are overlapped by other resonances. [e] These resonances were measured at −30 °C. At room temperature they appear broadened and partially overlapped owing to rotation around the Pt–olefin bond. [f] The coupling between the imine N=C*H* proton and the N-$CH_x(R)_{3-x}$ proton(s) is detectable ($^4J \approx 2$ Hz). [g] Pseudodoublets, belonging to a AA′XX′ multiplet, owing to accidental isochronism of the two methylene moieties. [h] AB quartet. [i] The spectrum was obtained from the equilibrium mixture with **9a′**, and the ethylene resonances are overlapped by those of **9a′**.

prompted to synthesize complexes of the type [PtClMe(η^2-olefin)(N-N′)]. We had two aims: first, to get thermodynamicly stable complexes and thus reversible addition–dissociation of the olefin, even with olefins not bearing electron-withdrawing substituents; secondly, in line with the current interest in chiral metal atoms,[14] to create a chiral center associated with the metal ion, taking advantage of the presence of five different substituents in the case of a complex with an unsymmetrical bidentate ligand. Some of the preliminary results concerning the synthesis of the complexes and the resolution of a chiral Pt(II) center appeared in a previous communication.[15]

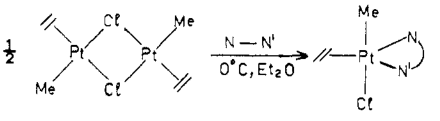
Results and Discussion

Synthesis and Characterization of the Five-Coordinate Complexes. A straightforward procedure for the synthesis of five-coordinate ethylene complexes of Pt(II) is the reaction of Zeise's dimer with the appropriate bidentate nitrogen ligand[7] (eq 1).



(1)

A recent report on the synthesis of a methyl derivative of Zeise's dimer[16] suggested to us the use of the above procedure as a way to obtain methyl-substituted five-coordinate complexes according to eq 2.[15] The products are



(2)

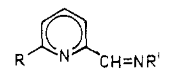
usually obtained in high yields as precipitates in diethyl ether. This reaction allows the preparation of complexes **a** with a large variety of nitrogen bidentates giving five-membered rings. The numbering used throughout this paper and the ^{1}H NMR data for a series of such compounds (**1a**–**10a**) are reported in Table I. Compounds,

$Me_2NN=C(Me)C(Me)=NNMe_2$
1

t-BuN=CHCH=N-*t*-Bu
2

$Me_2NCH_2CH_2NMe_2$
3

i-PrNHCH$_2$CH$_2$NH-*i*-Pr
4



	R	R′
5	H	Me
6	H	*t*-Bu
7	Me	Me
8	Me	CH_2Ph
9	Me	(S)-CH(Me)Ph
10	Me	*t*-Bu

---

(13) De Renzi, A.; Panunzi, A.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 535.

(14) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(15) De Renzi, A.; Morelli, G.; Panunzi, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1985**, *115*, 247. Presented in part at XII International Conference on Organometallic Chemistry, Vienna, 1985.

(16) Scott, J. D.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 193.

Table II. Selected ^{13}C NMR Data (δ),[a] IR Data,[b] and Ethylene Dissociation Constants for the Five-Coordinate Complexes [PtClMe(η^2-C_2H_4)(N-N′)]

compd	Pt–Me	N=CH or N—CH_2–	N–CH_xR_{3-x}	6-Me or 6-CH	CH_2CH_2	ν_{Pt-Cl}, cm^{-1}	K_{diss}
1a	−13.8 (662)		48.1		30.0 (358)	265	~10^{-5}
2a	−12.0 (662)	157.0	64.2 (34)		31.2 (370)	260	*c*
4a	−12.4 (723)	48.3 (13)	51.4 (8)		28.5 (375)		*c*
6a	−12.0 (664)	157.6	63.4 (30)	151.2 (47)	31.2 br (372)	250	4 × 10^{-2}
7a	−13.5 (668)	163.3	48.6 (49)	27.4 (12)	30.7 (370)	250	1.5 × 10^{-2}
8a	−13.0 (667)	161.8	65.1 (45)	27.4 (12)	31.1 br (360)	252	3.5 × 10^{-3}
9a′	−13.0 (662)	161.5	69.7 (38)	27.2 (20)	30.9 br (370)	250	~10^{-4}
9a″	−13.0 (662)	160.9	68.1 (42)	27.3 (20)	30.9 br (370)		
10a	−12.6 (667)	158.6	63.6 (29)	27.3 (13)	31.1 (370), 29.8 (370)	246	*c*

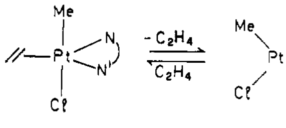
[a] $CDCl_3$, *T* = 30 °C, ^{195}Pt coupling constants (Hz) in parentheses. [b] Nujol mull. [c] No dissociation detectable.

which are not stable at room temperature (**3a**, **5a**), could be obtained by operating at temperatures below −30 °C.

Besides the analytical and conductivity data (the complexes are not conducting in chloroform), the assignment of a five-coordinate bipyramidal structure to complexes **a** can be made on the basis of ^1H and ^{13}C NMR data. Owing to the frequently found monodentate coordination of α-diimine ligands,[7,17] it is especially important to get unambigous evidence for the chelate binding mode in the case of complexes **a**. The main NMR features (see Tables I and II) pointing to the assigned structure are as follows: (a) coupling to ^{195}Pt of protons and/or carbons in both halves of the coordinated N-N ligands; (b) chemical equivalence of the two halves of the coordinated N-N ligand in the case of symmetric ligands; (c) chemical nonequivalence (below 0 °C) of all four ethylene protons in the case of unsymmetric N-N′ ligands; (d) large upfield shifts of the ethylene protons (1.7–3.0 ppm) and carbons (28–32 ppm), compared with the usual range for four-coordinate species (4.4–4.8 and 60–80 ppm, respectively).[7,9] Conditions a and b alone are not conclusive, since a monodentate N-N ligand with the two nitrogen atoms involved in fast exchange over the same platinum atom would give a similar result.[4a–7] Condition c alone is likewise not conclusive, since a monodentate N-N ligand in slow rotation around the Pt–N bond[18] would give the same result. However the simultaneous occurrence of conditions a and c, as found for complexes **5a**–**10a**, together with that of condition d, which was previously shown to be diagnostic of five-coordination for Pt(II) complexes,[7,9] can be assumed as conclusive evidence of a five-coordinate bipyramidal structure for complexes **a**.

A relevant feature of the NMR spectra of complexes **a** is that both olefinic ^1H and ^{13}C resonances appear in a significantly upfield range, compared with the corresponding dichloro complexes: ^1H, δ 1.7–3.0 in **1a**–**10a** vs. δ 3.3–3.7 in the dichloro complexes,[3-10] ^{13}C, δ 28.5–31.5 in **1a**–**10a** vs. 35.5–38.3 in the dichloro complexes.[9,10] An upfield shift in this range was also noted for the other five-coordinate ethylene methyl-platinum complexes reported in the literature[2b] and attributed to a substantial amount of π-back-bonding. If the correlation between upfield shifts of the olefinic protons and carbons and the extent of π-back-donation is valid,[2b] it can then be argued that the substitution of a chloride ion by the strongly donating methyl group results in an enhancement of the already relevant amount of π-back-bonding present in the five-coordinate complexes.

Dissociation–Association Equilibria and Four-Coordinate [PtClMe(N-N′)] Complexes. While the loss of ethylene by the five-coordinate dichloro complexes[3-10] is not reversible, many of the complexes **a** lose ethylene reversibly in solution converting to a four-coordinate species **b**, in an equilibrium (eq 3) which is strongly affected by the nature of the N-N′ ligand (see later).



a b

(3)

For complexes **6a**–**9a** the reaction proceeds smoothly at room temperature and can be easily monitored by ^1H NMR. By integration of the NMR signals of the equilibrium mixture in $CDCl_3$, approximate values for the equilibrium constant of the dissociation reaction could be determined and these are reported in Table II. We observed strong steric effects on the thermodynamic stability of complexes **a** with respect to loss of ethylene. These are mostly evident for the series of pyridinaldimines **5**–**10**. As the steric bulk on both sides of the ligand is increased, the stability continuously increases from complex **5a**, which irreversibly loses ethylene below 0 °C, to complex **10a**, which does not lose ethylene even in boiling chloroform. A similar influence of the steric demand of the N-N′ ligand on the kinetic stability of the analogous dichloro complexes was previously observed.[3,4,10]

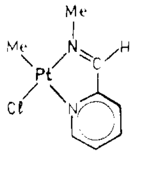
It is worth noting that, in the case of the unsymmetric ligands derived from the 2-pyridinealdehydes, the four-coordinate product can in principle consist of a pair of geometrical isomers. Only one isomer was actually obtained in most cases, and its configuration could be assigned on the basis of ^1H–^{195}Pt coupling constant data. As a manifestation of the high trans influence of the coordinated methyl group, the $^3J_{H-Pt}$ coupling constants for the ligand hydrogens close to the trans nitrogen are expected to be significantly lower than those for hydrogens close to the cis nitrogen,[19] reflecting a weaker Pt–N bond trans to the methyl group. The imine proton displays a ^{195}Pt coupling constant of about 100 Hz for complexes **7b**–**10b** and for the major isomer of complex **5b**, while the corresponding value is 37 Hz for **6b** and for the minor isomer of **5b**. Conversely, the 6-H resonance exhibits a ^{195}Pt coupling constant of 13 Hz for the major isomer of **5b**, while the corresponding value is 59 Hz for **6b** and for the minor isomer of **5b**. The observed inversion of magnitude of the quoted coupling constants going from $\mathbf{5b}_t$ and **6b** to $\mathbf{5b}_c$ and **7b**–**10b** can be ascribed to a change of configuration. The value of 100 Hz found for the imine H–Pt

---

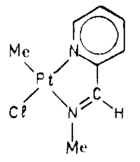
[17] van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

[18] Natile, G.; Cattalini, L.; Gasparrini, F. *J. Chem. Soc., Chem. Commun.* **1977**, 89.

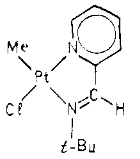
[19] (a) Clark, H. C.; Ward, J. E. H. *Can. J. Chem.* **1974**, *52*, 570. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.



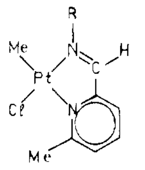
5b$_c$



5b$_t$



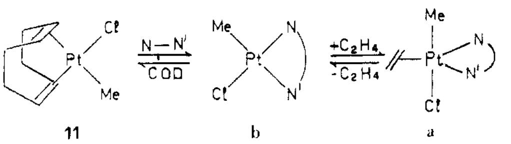
6b



	R
7b	Me
8b	CH_2Ph
9b	CH(Me)Ph
10b	*t*-Bu

coupling in **5b**$_c$ and **7b–10b** is the same, while the value of 13 Hz found for the pyridine 6-H–Pt coupling in **5b**$_c$ is much lower than those respectively reported for the corresponding dichloro complexes.[10] This result points to the imine nitrogen being cis to the methyl ligand in **5b**$_c$ and **7b–10b**, as unambigously confirmed by the X-ray structure in the case of **9b** (see later). The trans configuration can instead be assigned to **6b** and to the minor isomer of **5b** (**5b**$_t$). The geometric isomerism of the four-coordinate complexes is affected by the relative steric hindrance of both sides of the ligand. For the 6-methylpyridinaldimine complexes (**7b–10b**) a strong steric interaction is expected between the 6-methyl group and the cis ligand. Accordingly, all the complexes **7b–10b** consist of only one geometric isomer (the cis isomer), having the imine nitrogen cis to the methyl ligand. In absence of the 6-methyl group, the trans geometrical isomer, having the imine nitrogen trans to the methyl ligand, is obtained for **6b**, where the bulky *t*-Bu group is present on the imine nitrogen. A 10:1 cis to trans ratio is obtained for complex **5b**, where the imine nitrogen does not bear a bulky substituent. In the latter case, a reason for the preferential formation of the cis isomer, in the absence of special steric constraints, can be found in the preference for the weakest donor (the pyridine nitrogen) to locate trans to the strongest donor (the methyl ligand).

Alternative Synthesis of the Five-Coordinate Complexes. The reversibility of the ethylene dissociation reaction suggested to us an alternative way to obtain five-coordinate complexes **a** which are thermodynamically stable. The four-coordinate complexes **b** could first be prepared through an independent procedure and then converted to the complexes **a** by addition of ethylene. This was accomplished through a ligand displacement reaction, starting from the cyclooctadiene (COD) complex **11**,[11] with subsequent uptake of ethylene, according to eq 4.



(4)

11 b a

The type of reaction outlined in eq 4 could also be used for preparing five-coordinate olefin complexes bearing carbon ligands other than methyl.[20] However, besides its interest from a synthetic point of view, the essential features of the reaction allowed us to obtain relevant insights into the factors affecting the relative stabilities of the four- and five-coordinate complexes.

The reaction can be performed either in two separate steps, by first isolating the four-coordinate complex **b** and then reacting it with ethylene or in a single step under ethylene pressure. In the former case, we found that the displacement reaction took place only in a limited number of cases, i.e., for the synthesis of complexes **3b** and **5b–9b**. In cases where the displacement reaction was not favored, the five-coordinate complexes could nevertheless be obtained by performing the reaction in one step under ethylene atmosphere. Equilibrium mixtures of the product and the starting COD complex were obtained for **1a** and **2a** (both steps in eq 4 are actually reversible). In these cases yields could be improved by washing out the displaced COD and repeating the procedure.

The reactivity of different N-N′ ligands in the displacement reaction mirrors, in the opposite direction, the stability scale of the corresponding five-coordinate complexes with respect to loss of ethylene. *The more effective an N-N′ ligand in stabilizing the five-coordination, the less effective in displacing COD in the four-coordinate complex and vice versa.* As an example, the displacement reaction in hot toluene is very easy when N-N′ is 6-Hpy-2-CH=NMe (**5**), whose five-coordinate complex rapidly loses ethylene above −20 °C. It is sluggish with 6-Mepy-2-CH=NCH_2Ph (**8**) and 6-Mepy-2-CH=NCH(Me)Ph (**9**), which form five-coordinate complexes of moderate stability, and it does not take place at all with 6-Mepy-2-CH=N(*t*-Bu) (**10**), which forms a particularly stable five-coordinate complex.

Therefore, the stability of the five-coordinate complexes **a** with respect to loss of ethylene seems to be controlled by the *instability* of the corresponding four-coordinate complexes **b**. In other words, different five-coordinate complexes are expected to differ only slightly in energy on changing the ligand N-N′, while these differences should be much larger for the four-coordinate species **b**. We tested this idea with some ligand exchange experiments on the five-coordinate complexes **1a** and **7a**. When ligand **7** is added to complex **1a**, or ligand **1** to complex **7a** in chloroform solution, a ligand exchange reaction takes place, and an equilibrium is attained within 1 h at 25 °C, according to

$$\underset{\mathbf{1a}}{[PtCl(Me)(C_2H_4)(L\text{-}L)]} + \underset{\mathbf{7}}{L'\text{-}L'} \overset{K^{V}}{\rightleftharpoons} \underset{\mathbf{7a}}{[PtCl(Me)(C_2H_4)(L'\text{-}L')]} + \underset{\mathbf{1}}{L\text{-}L}$$

$$L\text{-}L = Me_2NN{=}C(Me)C(Me){=}NNMe_2;\quad L'\text{-}L' = 6\text{-Mepy-2-CH}{=}NMe$$

When the reaction is performed in an NMR tube, it could be readily monitored, and by integration of the ^1H NMR signals of the equilibrium mixture an approximate value of 7 could be determined for the equilibrium constant K^{V}.

The corresponding ligand exchange equilibrium constant K^{IV} for the four-coordinate complexes **1b** and **7b** was difficult to directly measure, since the reaction was extremely slow at room temperature, occurring through intermediates with the N-N ligands acting as monodentates. Nevertheless it is easy to see that the ratio K^{IV}/K^{V} can be indirectly determined, being equal to the ratio of the ethylene dissociation constants k_7/k_1 from complexes **7a** and **1a**, respectively. This leads to an estimate (see the dissociation constants reported in Table II) of not less than 10^3 for the equilibrium constant of the reaction

---

[20] De Felice, V.; Morelli, G.; Panunzi, A.; Vitagliano, A., manuscript in preparation.

$$\underset{\mathbf{1b}}{[\mathrm{PtCl(Me)(L\text{-}L)}]} + \underset{\mathbf{7}}{\mathrm{L'\text{-}L'}} \overset{K^{\mathrm{IV}}}{\rightleftharpoons} \underset{\mathbf{7b}}{[\mathrm{PtCl(Me)(L'\text{-}L')}]} + \underset{\mathbf{1}}{\mathrm{L\text{-}L}}$$

$$\mathrm{L\text{-}L = Me_2NN{=}C(Me)C(Me){=}NNMe_2;}$$
$$\mathrm{L'\text{-}L' = 6\text{-}Mepy\text{-}2\text{-}CH{=}NMe}$$

This result shows, in a semiquantitative way, one example of the above-mentioned concept that the stability of the four-coordinate species **b** is more sensitive to changes in the structure of the N-N′ ligand than that of the five-coordinate species **a**. This observation can be rationalized. Indeed, the structural data for platinum complexes show that the equatorial Pt–N bonds in trigonal-bipyramidal complexes are significantly longer (0.2–0.3 Å on the average) than Pt–N bonds in square-planar complexes (see later). If the Pt–N bonds are weaker in the trigonal-bipyramidal structure, the differences in bond strengths on changing the N–N′ ligand will also be smaller for five-coordinate complexes than for square-planar ones, in agreement with the above observations. Moreover, in the case of planar N-N′, interligand steric interactions in the coordination plane will be relevant for square-planar complexes but will be minimized for trigonal bipyramidal ones, thus amplifying stability differences between four-coordinate complexes with different N-N′ ligands. It has been already shown that increasing the steric hindrance on both sides of a planar N-N′ ligand increases the kinetic stability of five-coordinate species.[4b,10] Our results show that this holds also for the thermodynamic stability of the complexes.

Metal Chirality in the Five-Coordinate Complexes. As indicated in the Introduction, if the bidentate dinitrogen ligand is unsymmetrical, i.e., having two different halves, the platinum atom becomes a chiral center and can in principle be resolved through the coordination of an enantiomeric ligand. In view of further studies concerning the enantioselectivity in coordination of prochiral (or chiral) olefins to the chiral metal atom,[20] resolution was achieved by using the enantiomeric imine 6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph) (**9**).[15] As far as we know no other example of resolution of a chiral transition-metal atom in a trigonal-bipyramidal environment has been reported in the literature.

As shown by ^{1}H NMR (Table I), the crude product obtained through reaction 2 when N-N′ equals **9** consists of a 1:1 mixture of the two diastereomers **9a′** and **9a″**. This mixture epimerizes upon standing in solution to a final equilibrium composition of 63% **9a′** and 37% **9a″**. Following recrystallization from CH_2Cl_2–ether the mixture is almost quantitatively converted to crystals of pure **9a′** through a second-order asymmetric transformation.[15]

Several mechanisms are in principle possible for the epimerization reaction leading to the interconversion **9a′** ⇄ **9a″**, according to the different ways by which the bipyramidal platinum center could invert its configuration. A nondissociative mechanism could involve a pseudorotation with site exchange of N and N′.[21] In addition, three different dissociative paths are conceivable, involving release and then uptake of the olefin, the chloride ion, or one of the two nitrogen donors. More than one mechanism could also be operating at the same time, and a careful kinetic study should be done in order to discriminate among all the possibilities. We tend however to favor the direct olefin dissociation and/or the bidentate–unidentate interconversion of the N–N′ ligand as the most likely paths for the configurational inversion at platinum. The former equilibrium (**9a** ⇄ **9b** + C_2H_4) is in fact detectable in solution in the present case, and the latter has been observed for analogous dichloro complexes.[4,7,9] It is significant that in the case of prochiral olefins, the dissociation–association equilibrium would also provide a way for the configurational inversion of the coordinated olefin. This would allow the equilibration of a diastereomeric mixture and thus the attainment of asymmetry induction effects, directed from a chiral N–N′ ligand such as **9** to the coordinated olefin, possibly mediated by the metal chirality. Such an asymmetry induction effect was *not* actually observed for the five-coordinate dichloro complex [$PtCl_2$(styrene)(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph))], which was reported to consist of a 1:1 mixture of two diastereomeric species.[10] Since the dichloro complexes [$PtCl_2$(olefin)(6-Mepy-2-CH=NR)] were found to be resistant to olefin exchange,[4b,10] the reason for the lack of asymmetry induction in the styrene dichloro complex of **9** could be the lack of a low-energy path for the equilibration of the 1:1 diastereomeric mixture. Studies concerning the mutual effects of asymmetry induction between a chiral N-N′ ligand, the metal chiral center, and a prochiral olefin are presently in progress in our laboratory.

Table III. Crystal Data and Details of Measurements for 9b and 9a′

	9b	9a′
formula	$C_{16}H_{19}ClN_2Pt$	$C_{18}H_{23}ClN_2Pt$
fw	469.9	497.9
cryst system	orthorombic	monoclinic
a, Å	9.354 (1)	8.524 (1)
b, Å	10.555 (2)	10.921 (2)
c, Å	16.290 (1)	10.017 (1)
β, deg	90	105.20 (1)
V, Å^3	1608.2	899.8
d_{calcd}, g/cm^3	1.94	1.84
Z	4	2
space group	$P2_12_12_1$	$P2_1$
F(000)	896	457
cryst color	dark red	orange-yellow
cryst size, mm	0.1 × 0.1 × 0.05	0.15 × 0.1 × 0.4
μ(Mo Kα), cm^{-1}	89.72	80.23
θ range, deg	2.5–30	2.5–30
scan type	$\omega/2\theta$	$\omega/2\theta$
scan interval, deg (+0.35 tan θ)	0.8	0.7
prescan speed, deg/min	8	8
prescan acceptance [$\sigma(I)/I$]	0.5	0.5
required final $\sigma(I)/I$	0.01	0.01
max time, s	140	140
collected octants	+*h*, +*k*, +*l*	±*h*, +*k*, +*l*
no. of indep data	2673	2882
no. of obsd refls ($I > 2\sigma(I)$)	1695	2393
transmissn range	86–100	73–100
R, R_w	0.021, 0.023	0.020, 0.020
K, *g*	0.8, 0.007	1.0, 0.0071

Molecular Structures of [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph))] (9b) and [PtClMe(C_2H_4)(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph))] (9a′). In order to get at the same time a full structural characterization for the class **a** complexes, insight into the structural factors affecting the stability of five-coordinate species, and a stereochemical characterization of a chiral metal ion in a trigonal-bipyramidal geometry, we undertook X-ray structural investigations of complexes **9b** and **9a′**, related to each other by the uptake and loss of ethylene. Crystal data and atomic coordinates for the two complexes are reported in Tables III–V.

Four-Coordinate Complex 9b. The crystal contains units [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph))], depicted in Figure 1. Relevant bond distances and angles are reported in Table VI. The platinum atom exhibits the expected square-planar coordination with two cis

---

(21) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

Table IV. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)] (9b)

atom	x	y	z	U_{iso} or U_{eq}, Å^2
Pt	0.30293 (2)	−0.00782 (2)	0.31679 (1)	0.0440 (1)
Cl	0.2078 (2)	0.0213 (2)	0.4449 (1)	0.081 (1)
N(1)	0.1958 (6)	0.1430 (4)	0.2453 (3)	0.044 (3)
N(2)	0.3953 (6)	−0.0283 (5)	0.2074 (3)	0.044 (2)
C(1)	0.0899 (8)	0.2247 (7)	0.2628 (5)	0.057 (4)
C(2)	0.0452 (9)	0.3116 (7)	0.2021 (5)	0.066 (5)
C(3)	0.0993 (9)	0.3144 (7)	0.1255 (5)	0.064 (4)
C(4)	0.2088 (9)	0.2290 (7)	0.1080 (4)	0.060 (4)
C(5)	0.2533 (7)	0.1474 (6)	0.1679 (4)	0.050 (4)
C(6)	0.0245 (10)	0.2259 (9)	0.3465 (5)	0.081 (6)
C(7)	0.3609 (8)	0.0516 (7)	0.1510 (4)	0.051 (4)
C(8)	0.4997 (7)	−0.1289 (6)	0.1839 (4)	0.052 (3)
C(9)	0.4160 (11)	−0.2371 (8)	0.1440 (6)	0.078 (6)
C(10)	0.6233 (7)	−0.0797 (6)	0.1337 (4)	0.048 (4)
C(11)	0.7253 (10)	−0.0053 (8)	0.1742 (5)	0.075 (5)
C(12)	0.8402 (11)	0.0413 (10)	0.1296 (9)	0.105 (8)
C(13)	0.8530 (12)	0.0154 (11)	0.0478 (8)	0.108 (8)
C(14)	0.7530 (12)	−0.0555 (11)	0.0095 (6)	0.092 (7)
C(15)	0.6400 (9)	−0.1009 (8)	0.0512 (5)	0.069 (5)
C(16)	0.4135 (9)	−0.1542 (7)	0.3689 (4)	0.067 (4)

Table V. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for [PtClMe(η^2-C_2H_4)(6-Mepy-2-CH=N-(*S*)-CH(Me)Ph)] (9a′)

atom	x	y	z	U_{iso} or U_{eq}, Å^2
Pt	0.24183 (1)	0.25000	0.20955 (1)	0.0350 (1)
Cl	0.4397 (2)	0.0814 (1)	0.2566 (2)	0.059 (1)
N(1)	0.1592 (5)	0.1984 (4)	0.3964 (5)	0.043 (2)
N(2)	0.3932 (5)	0.3557 (4)	0.3813 (4)	0.041 (2)
C(1)	0.0373 (9)	0.1214 (7)	0.4001 (7)	0.061 (4)
C(2)	−0.0059 (9)	0.1016 (8)	0.5230 (8)	0.068 (4)
C(3)	0.0714 (8)	0.1622 (8)	0.6395 (7)	0.070 (4)
C(4)	0.1967 (7)	0.2482 (12)	0.6382 (5)	0.064 (3)
C(5)	0.2339 (5)	0.2593 (10)	0.5114 (4)	0.042 (2)
C(6)	−0.0401 (13)	0.0505 (11)	0.2705 (10)	0.096 (6)
C(7)	0.3613 (6)	0.3443 (5)	0.5000 (5)	0.042 (2)
C(8)	0.5253 (6)	0.4410 (6)	0.3697 (7)	0.052 (3)
C(9)	0.6526 (8)	0.3670 (9)	0.3224 (12)	0.083 (5)
C(10)	0.4507 (6)	0.5450 (6)	0.2780 (6)	0.048 (3)
C(11)	0.3823 (7)	0.6389 (6)	0.3372 (8)	0.058 (3)
C(12)	0.3124 (10)	0.7419 (15)	0.2618 (12)	0.080 (5)
C(13)	0.3119 (11)	0.7482 (16)	0.1207 (14)	0.098 (7)
C(14)	0.3798 (14)	0.6484 (15)	0.0594 (12)	0.110 (8)
C(15)	0.4453 (11)	0.5482 (10)	0.1370 (8)	0.076 (5)
C(16)	0.0708 (6)	0.3873 (6)	0.1712 (6)	0.054 (3)
C(17)	0.1392 (9)	0.1792 (7)	0.0166 (6)	0.058 (3)
C(18)	0.2566 (7)	0.2687 (8)	0.0090 (5)	0.051 (3)

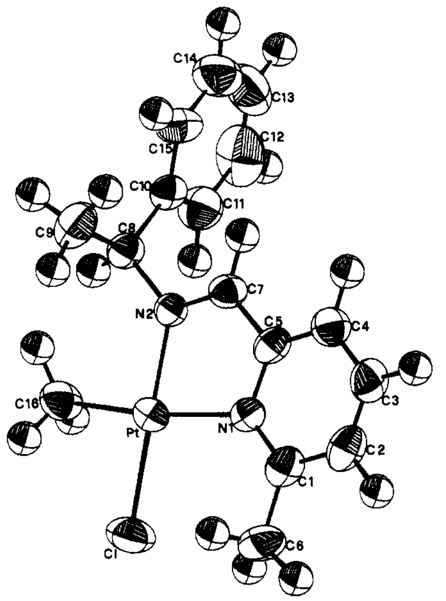


Figure 1. ORTEP view of [PtClMe(6-Mepy-2-CH=N-(*S*)-CH(Me)(Ph))] (**9b**). Thermal ellipsoids are drawn at the 50% probability level.

Table VI. Bond Distances (Å) and Relevant Angles (deg) for 9b and 9a′

	9b	9a′
	Bond Distances	
Pt–Cl	2.290 (2)	2.457 (2)
Pt–N(1)	2.213 (5)	2.239 (5)
Pt–N(2)	1.993 (5)	2.188 (4)
Pt–C(16)	2.044 (8)	2.055 (6)
N(1)–C(1)	1.34 (1)	1.35 (1)
C(1)–C(2)	1.41 (1)	1.39 (1)
C(2)–C(3)	1.35 (1)	1.35 (1)
C(3)–C(4)	1.39 (1)	1.43 (1)
C(4)–C(5)	1.37 (1)	1.39 (1)
N(1)–C(5)	1.37 (1)	1.34 (1)
C(1)–C(6)	1.49 (1)	1.51 (1)
C(5)–C(7)	1.45 (1)	1.46 (1)
N(2)–C(7)	1.29 (1)	1.29 (1)
N(2)–C(8)	1.49 (1)	1.49 (1)
C(8)–C(9)	1.53 (1)	1.53 (1)
C(8)–C(10)	1.51 (1)	1.49 (1)
C(10)–C(11)	1.40 (1)	1.39 (1)
C(11)–C(12)	1.39 (2)	1.40 (2)
C(12)–C(13)	1.37 (2)	1.41 (2)
C(13)–C(14)	1.35 (2)	1.45 (2)
C(14)–C(15)	1.35 (1)	1.37 (2)
C(10)–C(15)	1.37 (1)	1.40 (1)
Pt–C(17)		2.051 (6)
Pt–C(18)		2.056 (6)
C(17)–C(18)		1.42 (1)
	Bond Angles	
N(1)–Pt–N(2)	78.7 (2)	74.1 (2)
C(16)–Pt–Cl	85.4 (2)	178.2 (2)
Pt–N(1)–C(1)	133.1 (5)	126.6 (4)
N(1)–C(1)–C(6)	120.1 (7)	117.6 (8)
Pt–N(1)–C(5)	109.3 (4)	114.3 (4)
N(1)–C(5)–C(7)	115.0 (6)	116.4 (4)
C(5)–C(7)–N(2)	119.6 (6)	118.4 (4)
C(7)–N(2)–Pt	117.3 (4)	116.7 (3)
Pt–N(2)–C(8)	126.1 (4)	124.7 (6)
Cl–Pt–N(1)	102.0 (1)	
N(2)–Pt–C(16)	94.0 (2)	

positions occupied by the pyridinic (N(1)) and iminic (N(2)) atoms and the methyl (C(16)) and chloride ligands trans to N(1) and N(2), respectively. The atoms defining the coordination plane are strictly coplanar (maximum deviation from the average plane, 0.04 Å). The bidentate ligand is flat and almost coplanar with the coordination plane (maximum deviation from the average plane, 0.08 Å; dihedral angle between planes, 4°). Among the two possible isomers the actual one seems to be sterically favored because close contacts are avoided between the coordinated and pyridinic methyl groups. On the other hand, electronic factors can play a role because of the different basicity of the pyridinic and iminic nitrogen atoms (see previous sections). The bond angles at platinum show distortions that in part can be attributed to interligand steric tensions. The more significant deviations are generated by the constraints of the chelate ring. The acute bite angle N(1)–Pt–N(2) of 78.7 (2)° is mainly responsible for the obtuse angle N(1)–Pt–Cl (102.0 (1)°), as confirmed by the almost ideal value for N(2)–Pt–Cl (177.0 (2)°). The bond angles in the vicinity of the chloride ligand show a limited evidence of strain; nevertheless this ligand is in close contact with the contiguous methyl groups (Cl···C(16) = 2.9 Å and Cl···C(6) = 3.2 Å). The slight closure of the Cl–Pt–C(16) angle (85.4 (2)°) is mainly the consequence of the opening of the N(2)–Pt–C(16) angle (94.0 (3)°). The latter value and the accompanying widening of Pt–N-

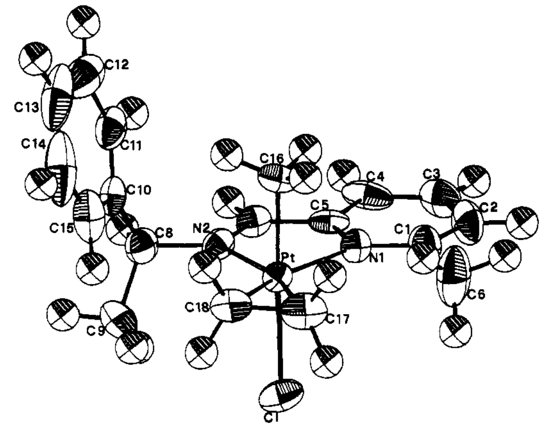


Figure 2. ORTEP view of $[PtClMe(C_2H_4)(6\text{-Mepy-2-CH=N-}(S)\text{-CH(Me)(Ph)})]$ (**9a′**). Thermal ellipsoids are drawn at the 50% probability level.

(2)-C(8) (126.1 (4)°) alleviate interhydrogen contacts. It is expected that higher branching at C(8) would produce higher steric tension in this region of the molecule (vide infra). The significant deviation from linearity of the atoms C(16)-Pt-N(1) (172.6 (2)°) suggests that the Pt-N(1) bond is slightly bent. As ring constraints do not allow ideal overlap of the platinum orbitals with both nitrogen lone pairs, some tension must be present in these bonds. The just discussed angular values indicate that in the present case the orbital mismatching is not averaged on the two Pt-N interactions but it is charged on the weaker N(1)-Pt bond which is 0.22 Å longer than N(2)-Pt (2.213 (5) vs. 1.993 (5) Å). This effect is even more evident if one compares the almost ideal angle C(7)-N(2)-Pt (117.3 (4)°) with C(5)-N(1)-Pt (109.3 (4)°). The latter value clearly indicates that the lone pair at N(1) is directed some 10° off the N(1)-Pt vector. The destabilization of the Pt-N(1) interaction, determined by the strong trans influence of the methyl ligand, causes the preferential bending of this bond. The geometrical evidence of the methyl group's trans influence is consistent with the previously mentioned decrease in $^3J_{H-Pt}$ coupling constants going from protons close to the imine nitrogen to protons close to the pyridine nitrogen.

The N(2)-Pt distance (1.993 (5) Å) is quite short and, if compared with the values found for the imine nitrogens in the square-planar species *trans*-$[PtCl_2(C_2H_4)(Me_2CHN{=}CHCH{=}NNMe_2)]$ (2.031 (5)Å) and *trans*-$[PtCl_2(E\text{-}MeCH{=}CHMe)(t\text{-}BuN{=}CHCH{=}N\text{-}t\text{-}Bu)]$ (2.07 (1) Å),[7] shows that some back-bonding can be operating from platinum to the π^*-delocalized orbitals of the chelate ligand. The Pt-Cl distance (2.290 (2) Å) is normal and strictly equivalent to the values found in the just mentioned species.[7]

Five-Coordinate Complex 9a′. The molecular structure of **9a′** is depicted in Figure 2; bond distances and relevant angles are reported in Table VI. The platinum atom exhibits the expected trigonal-bipyramidal coordination geometry with methyl and chloride ligands in axial position (C(16)-Pt-Cl angle = 178.2 (2)°). The bidentate N-N′ ligand and the ethylene molecule are in the equatorial plane (maximum deviation from the coordination plane, 0.04 Å). The bidentate ligand is flat with the obvious exception of the residues bonded to the chiral center C(8) (maximum deviation from the average plane, 0.015 Å; dihedral angle with the equatorial plane, 4°). The platinum atom is a center of chirality and has C (clockwise) absolute configuration.[22] On inspecting Figure 2 one can see that the stability of this diastereomer with respect to the one with inverted axial ligands is influenced by the chiral center C(8) mainly through the rotation of the CHMePh fragment around the N(2)-C(8) axis. This residue is actually conformed with the hydrogen atom near the equatorial plane and pointing opposite to the ethylene ligand. The methyl and phenyl groups are placed on opposite sides of the coordination plane in such a way as to keep the methyl ligand C(16) far from the methyl C(9). One should note that the CHMePh fragment is differently conformed in the square-planar complex **9b** (Figure 1), being rotated by about 60° away from the present position.

The ethylene molecule is symmetrically coordinated with bond parameters Pt—C and C=C equal to 2.053 (6) and 1.415 (11) Å, respectively. These values can be compared with those recently found in the five-coordinate $[PtCl_2(C_2H_4)(Me_2NN{=}CHCH{=}NNMe_2)]$, 2.10 (2) and 1.50 (2) Å.[23] Interestingly, the values found in four-coordinate complexes are generally indicative of weaker bond interactions, e.g., 2.173 (7) and 1.40 (1) Å, in $[PtCl_2(C_2H_4)(Me_2CHN{=}CHCH{=}NNMe_2)]$.[7] These values show that the strength of the platinum-olefin interaction is strongly dependent on the back-bonding ability of the metal which increases from four- to five-coordinate species and, among the latters, is greater in methyl chloro than in dichloro derivatives. These observations are consistent with the upfield shift of the ^1H and ^{13}C olefinic resonances in the present species with respect to the analogous dichloro complexes.

The Pt-N distances are slightly but significantly different: Pt-N(1) (pyridine N) = 2.239 (5) and Pt-N(2) (imine N) = 2.188(5) Å. Being these atoms in geometrically equivalent positions, the 0.05-Å difference in bond lengths is indicative of the different bonding abilities of the two types of nitrogen atoms. A comparison of the Pt-N(2) distance with the corresponding one in **9b** (2.188 (4) vs. 1.993 (5) Å) shows a 0.2-Å lengthening for the five-coordinate species that can be attributed to causes comprising the higher electron density at the platinum atom and a less favourable orbital overlap in the equator of the trigonal-bipyramidal with respect to the square-planar geometry. The value found for the bis(hydrazone) ligand in $[PtCl_2(MeCH{=}CHMe)(Me_2NN{=}C(Me)C(Me){=}NNMe_2)]$ (2.24 (1) Å)[24] is substantially coincident with the Pt-N(1) (pyridine N) distance, but when the ligand is a diamine, in which no delocalized π^* orbitals are present, the Pt-N distances are at a maximum, e.g., 2.37 (1) Å in $[PtCl_2(C_2H_4)(PhMeCHN(Me)CH_2CH_2N(Me)CHMePh)]$.[3b] These observations show the importance of the metal-to-ligand back-bonding whenever suitable orbitals exist.

The Pt-Me distance (2.055 (6) Å) is substantially equivalent to the value in the four-coordinate complex **9b** (2.044 (8) Å) and to the Pt-C(olefin) distance (2.053 (6) Å). On the contrary, the Pt-Cl distance is longer than that in the four-coordinate **9b** (2.457 (2) vs. 2.290 (2) Å). The lengthening is due to the strong trans influence of the methyl group that was already noticed in **9b** and is consistent with the low Pt-Cl stretching frequencies in the IR spectra of complexes **a** (Table II) and with the easy substitution of the chloride ligand in the presence of silver ions to give cationic complexes.[15]

---

(22) Sloan, T. E. In *Topics in Inorganic and Organometallic Stereochemistry*; Geoffroy, G. L., Ed.; Wiley-Interscience: New York, 1981; pp 1-36.

(23) Bavoso, A.; Funicello, M.; Morelli, G.; Pavone, V. *Acta Cryst* **1984**, *C40*, 2035 and references therein.

(24) Albano, V. G.; Demartin, F.; Di Blasio, B.; Morelli, G.; Panunzi, A. *Gazz. Chim. Ital.* **1985**, *115*, 361.

After an analysis of the geometries of **9b** and **9a′** one looks for clues explaining the fact that the stabilities of five-coordinate species with respect to the loss of ethylene decrease on reducing the branching at C(8) and even more on removing the C(6) methyl group, as indicated by the approximate ethylene dissociation constants (Table II). The present results are not conclusive in this respect because structural data on other related species would be necessary. Nevertheless it is evident that an alleviation of the interligand contacts takes place on rearranging the molecular geometry from square planar to trigonal bipyramidal, and the consequent enthalpic gain should be proportional to the hindrance of the bidentate ligand.[25]

Conclusions

The reversibility of the olefin dissociation from five-coordinate dichloro complexes $[PtCl_2(\eta^2\text{-olefin})(N\text{-}N')]$ was never observed,[3-10] while it is a remarkable property of the methyl derivatives $[PtClMe(\eta^2\text{-}C_2H_4)(N\text{-}N')]$ reported in this paper. This makes complexes **a** good substrates for investigating the factors affecting the thermodynamic stability of five-coordinate species. Moreover, the use of complexes of this type for the investigation of asymmetry induction effects in the coordination of prochiral olefins to a chiral metal center can be anticipated.

Concerning the effect of the chelating ligand on the stability of the five-coordinate complexes, the reported results suggest that an important factor affecting the olefin dissociation equilibrium is the steric hindrance present in the coordination plane on both sides of the bidentate N-N′ ligand. As this increases, the four-coordinate species is destabilized by the repulsive interactions of the substituents on N and N′ with the cis ligands, resulting in a stabilization of the corresponding five-coordinate complex. This effect can be easily rationalized in case of all-planar, sp^2-hybridized N-N′ ligands, like **1**, **2**, and **5**–**10**, and should probably allow a qualitative forecast of the stability of a given five-coordinate complex of this type. In the case of ligands where the steric bulk is not acting in the coordination plane, like the diamines, such rationalization appears to be more difficult. A repulsive interaction between the substituents on N and N′ and the axial ligands of the five-coordinate complex can be present in this case, thus complicating the balance of steric effects in the interconversion from the trigonal-bipyramidal geometry to the square-planar one.

Experimental Section

^{1}H NMR spectra were recorded at 60 and 270 MHz on a Varian T-60 A and on a Brucker WH 270 spectrometer, respectively. ^{13}C NMR spectra were recorded at 50.3 MHz on a Varian XL 200 spectrometer. $CDCl_3$ was used as solvent and tetramethylsilane as internal standard.

IR spectra were recorded in Nujol mull on a Perkin-Elmer 457 spectrophotometer using CsI windows.

Solvents and reagents were of AnalaR grade. Unless otherwise stated, they were used without further purification. N-N′ ligands were prepared and stored under nitrogen. Unless otherwise stated, platinum complexes were prepared and stored in air.

Materials. Ligand **3** is commercially available. Ligands **1**,[26] **2**,[27] and **4**[3a] were synthesized as previously described. Ligands **5**–**10** were prepared by 1:1 molar ratio condensation of the appropriate aldehyde and primary amine.[10] The starting platinum complexes $[PtClMe(C_2H_4)]_2$[16] and $[PtClMe(COD)]$ (**11**)[11] were prepared as previously described. The former was handled under nitrogen atmosphere and stored at −30 °C.

Synthesis of $[PtClMe(\eta^2\text{-}C_2H_4)(N\text{-}N')]$ Complexes. 1a, 2a, 4a, 6a, 7a, 8a, 9a, and 10a. The chloride-bridged dimer $[PtClMe(C_2H_4)]_2$ was suspended (partially dissolved) in anhydrous diethyl ether (0.5 mmol/mL) at 0 °C under ethylene atmosphere. A 10% molar excess (based on Pt content) of the appropriate N-N ligand was added under stirring, and a colorless (**4a**), orange (**1a**), or yellow precipitate was formed. After the suspension was stirred under ethylene atmosphere for 30 min, the precipitate was collected on a filter and dried, giving the required $[PtClMe(\eta^2\text{-}C_2H_4)(N\text{-}N)]$ complex in 80–90% yield.

3a and 5a. The same procedure as above was used, at a lower temperature (−30 °C).

All complexes could be recrystallized from CH_2Cl_2–diethyl ether (ethylene atmosphere for **6a**–**8a**) except **3a** and **5a**, which are thermally unstable and irreversibly dissociate. Elemental analyses (C, H, and N) were performed for all complexes, except **3a** and **5a**). Anal. Calcd for $C_{11}H_{25}N_4ClPt$ (**1a**): C, 29.76; H, 5.68; N, 12.62. Found: C, 29.62; H, 5.71; N, 12.48; Calcd for $C_{13}H_{27}N_2ClPt$ (**2a**): C, 35.33; H, 6.16; N, 6.34. Found: C, 35.11; H, 6.31; N, 6.26. Calcd for $C_{11}H_{27}N_2ClPt$ (**4a**): C, 31.62; H, 6.51; N, 6.70. Found: C, 31.38; H, 6.78; N, 6.56. Calcd for $C_{13}H_{21}N_2ClPt$ (**6a**): C, 35.82; H, 4.86; N, 6.43. Found: C, 36.02; H, 5.03; N, 6.39. Calcd for $C_{11}H_{17}N_2ClPt$ (**7a**): C, 32.40; H, 4.20; N, 6.87. Found: C, 32.21; H, 4.37; N, 6.82. Calcd for $C_{17}H_{21}N_2ClPt$ (**8a**): C, 42.20; H, 4.37; N, 5.79. Found: C, 42.05; H, 4.71; N, 5.86. Calcd for $C_{18}H_{23}N_2ClPt$ (**9a′**): C, 43.42; H, 4.66; N, 5.63. Found: C, 43.35; H, 4.73; N, 5.59. Calcd for $C_{14}H_{23}N_2ClPt$ (**10a**): C, 37.38; H, 5.15; N, 6.23. Found: C, 37.28; H, 5.43; N, 6.14.

Synthesis of $[PtClMe(N\text{-}N')]$ Complexes by Dissociation of $[PtClMe(C_2H_4)(N\text{-}N')]$ Complexes. The decomposition of **5a** to give **5b** was very fast in methylene chloride at room temperature. For the other complexes a chloroform solution (**1b**) or methylene chloride solution (**3b**, **6b**, **7b**, **8b**, **9b**) of the appropriate five-coordinate complex (0.1 mmol/mL) was boiled to dryness at atmospheric pressure, and the procedure was repeated twice (four times in case of **1b**). The required complex was obtained in essentially quantitative yields as a brown-red residue (colorless in case of **3b**) which could be recrystallized from CH_2Cl_2–diethyl ether. Anal. Calcd for $C_9H_{21}N_4ClPt$ (**1b**): C, 26.00; H, 5.09; N, 13.47. Found: C, 26.03; H, 5.20; N, 13.30. Calcd for $C_7H_{19}N_2ClPt$ (**3b**): C, 23.24; H, 5.29; N, 7.74. Found: C, 22.97; H, 5.54; N, 7.68. Calcd for $C_8H_{11}N_2ClPt$ (**5b**): C, 26.27; H, 3.03; N, 7.66. Found: C, 26.28; H, 3.12; N, 7.50. Calcd for $C_{11}H_{17}N_2ClPt$ (**6b**): C, 32.40; H, 4.20; N, 6.87. Found: C, 32.34; H, 4.23; N, 6.92. Calcd for $C_9H_{13}N_2ClPt$ (**7b**): C, 28.46; H, 3.45; N, 7.38. Found: C, 28.13; H, 3.52; N, 7.22. Calcd for $C_{15}H_{17}N_2ClPt$ (**8b**): C, 39.52; H, 3.76; N, 6.14. Found: C, 39.67; H, 3.64; N, 6.01. Calcd for $C_{16}H_{19}N_2ClPt$ (**9b**): C, 40.90; H, 4.08; N, 5.96. Found: C, 40.77; H, 4.31; N, 6.06. Some attempts to prepare the four-coordinate complexes with N-N′, **2**, **4**, and **10**, through a similar procedure failed, the starting five-coordinate complexes **2a**, **4a**, and **10a** being recovered almost unaltered. More drastic treatment (prolonged boiling in toluene) resulted in decomposition to metallic platinum and unidentified products.

Synthesis of $[PtClMe(N\text{-}N')]$ Complexes by Ligand Displacement from $[PtClMe(COD)]$. 3b. To a chloroform solution of the cyclooctadiene complex **11** (200 mg/3 mL) was added an excess (0.15 mL) of tetramethylethanediamine (**3**), and the solution was kept at room temperature for 48 h. The solvent was evaporated in vacuo, and the residue was crystallized from CH_2Cl_2–diethyl ether, giving 160 mg (78% yield) of the required

---

[25] In case the ethylene dissociation is a one-step concerted process, some correlation between the expected kinetic stabilities of the five-coordinate species and the hindrance of the bidentate ligand is also possible. In fact, after ethylene dissociation, the rearrangement of the four-coordinate fragment to the stable planar geometry can be strongly affected. The migration of the methyl and chloride ligands from axial to equatorial sites can proceed straightforwardly for ligands not bearing side groups and with increasing difficulty on increasing the hindrance at C(1) and C(8). In the present case the ligand migration is obliged to proceed in the direction leading C(16) far from C(6) and must be accompanied by a concerted rotation of the CHMePh grouping. Therefore, the higher the ligand hindrance, the slower the rearrangement process and the higher the probability the ethylene reenters the coordination site. The influence of this type of factors on the kinetic stability of complexes **a** deserves further investigations.

[26] Bock, H.; tom Dieck, H. *Chem. Ber.* **1967**, *100*, 228.

[27] Exner, O.; Kliegman, J. M. *J. Org. Chem.* **1971**, *36*, 2014. tom Dieck, H.; Renk, I. W. *Chem. Ber.* **1971**, *104*, 110.

complex as a colorless solid. **5b and 6b.** The cyclooctadiene complex 11 was dissolved in toluene (0.2 mmol/mL) at 80 °C, and a 2:1 molar excess of the appropriate ligand was added. The solution turned rapidly to a deep red and a brown-red solid crystallized after a few minutes. The mixture was cooled at room temperature, and the resulting crop of crystals was collected (75% yield). A second crop could be obtained by concentration of the filtrate and addition of diethyl ether. **7b.** [PtClMe(COD)] (11) (750 mg, 2.12 mmol) was dissolved in 10 mL of hot toluene, and 570 mg (4.25 mmol) of 6-Mepy-2-CH=NMe (7) was added. The solution was refluxed for 10 min, and after the solution was cooled to room temperature, the resulting crop of crystals was collected, giving 630 mg of a 3:2 mixture of **7a** and of the starting complex 11 (abundances determined by ^{1}H NMR of the mixture). A further crop of 140 mg was obtained by concentrating the filtrate and adding diethyl ether (1:2 mixture of **7a** and the starting cyclooctadiene complex). The two combined fractions were dissolved again in hot toluene (6 mL), and 400 mg of 6-Mepy-2-CH=NMe (7) was added. The mixture was refluxed for 5 min, and after the mixture was cooled at room temperature, 560 mg of purple crystals was isolated, consisting of essentially pure **7a** (66% yield). **8b and 9b.** The same procedure as above gave very poor yields of the required complexes. The reason for this is an unfavorable equilibrium constant for the displacement reaction. Indeed, by adding a slight excess of cyclooctadiene to a sample of **9b** in $CDCl_3$ at 40 °C, the reverse reaction took place, and after a few hours the ^{1}H NMR spectrum of the solution showed that the diimine 9 had almost completely been displaced by the diene, giving [PtClMe(COD)] (11). **1b.** This complex could not be obtained by displacement of cyclooctadiene in 11 (in a test experiment, the reverse reaction was quantitative). Similarly, ligands 2, 4, and 10 were not able to displace the diene in 11.

Synthesis of [PtClMe(η^2-C_2H_4)(N-N′)] Complexes by Ethylene-Assisted Ligand Displacement from [PtClMe(COD)]. 4a, 8a, 9a, and 10a. To a chloroform solution of the cyclooctadiene complex 11 (0.2 mmol/mL) was added a 20% molar excess of the appropriate N-N ligand, and the solution was stirred under a 2 atm of ethylene pressure for 24 h at room temperature. By concentration to a small volume and addition of diethyl ether the required complex was obtained in 80–90% yield (70% in case of **4a**). **1a and 2a.** The same procedure as above gave poor yields (10–20%) of complexes **1a** and **2a**, which were obtained in mixture with the starting cyclooctadiene complex 11. Yields could be improved by using a large excess of the N–N ligand (5:1 molar ratio) and repeating the procedure. The reason for the low yield of the reaction is clearly its unfavorable overall equilibrium constant. Indeed, addition of an excess of cyclooctadiene to a sample of pure **1a** or **2a** in $CHCl_3$ at room temperature resulted in a quantitative displacement of ethylene and of the N–N ligand, giving [PtClMe(COD)] (11).

Equilibrium Constants of the Ethylene Dissociation Reaction. 6a, 7a, and 8a. To a $CDCl_3$ solution of the complex (0.100 mmol/mL) was added free ethylene (about 0.05 mmol/mL) in a gas-tighted NMR tube, and the solution was allowed to equilibrate by standing 24 h at room temperature. The ^{1}H NMR spectrum (270 MHz) of the solution was recorded, and the relative concentrations of complexes **a** and **b**, and of free ethylene, were measured by integration of the corresponding signals, thus allowing the equilibrium constant to be calculated. No appreciable change in the NMR spectrum was observed after a further 6 h. **1a and 9a.** The same procedure as above was used, except that a more diluted (0.02 mmol/mL) solution was used and no free ethylene was added, in order to get an appreciable dissociation.

Since quantitative measurements were only done at a single metal and ethylene concentration for each complex, the estimated values of the dissociation constant (Table II) are grossly tentative. However, their fairly wide variations on changing the N-N′ ligand make them fully significant for the qualitative conclusions which are drawn in this paper.

X-ray Structural Determination of 9b and 9a′. Crystals suitable for X-ray analyses were obtained by recrystallization from methanol–diethyl ether (**9b**) and from methylene chloride–diethyl ether (**9a′**). Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, reduced to F_o values and corrected for crystal decay. Empirical absorption correction was applied to both data sets by measuring azimutal reflections ($\chi > 80°$). Crystal data and experimental details are compiled in Table III.

Both structures were solved by conventional Patterson methods and refined by full-matrix least squares, the minimized function being $\sum w|F_o - F_c|^2$. The weighting scheme employed was $w = K/[\sigma^2 + |g|F^2]$ where both K and g were optimized (see Table III). The SHELX package of crystallographic programs[28] was used for all calculations with the scattering factors, corrected for real and imaginary parts of anomalous dispersion, taken from ref 29. Thermal vibrations were treated anisotropically for all non-hydrogen atoms. H atoms were added in calculated positions and not refined though their contribution to the structure factors was taken into account. Highly significant differences in R values were found for the enantiomeric models of both **9b** and **9a′**, as one can see by comparing the R and R_w indexes in Table III with the values for the rejected models: 0.025 and 0.027 for **9b** and 0.026 and 0.027 for **9a′**. The crystallographic determination of the absolute configuration fully confirmed the known configuration of the chiral center in the bidentate N-N′ ligand. Final difference Fourier maps were computed and revealed residual peaks of less than 1 e Å^{-3} in proximity of the Pt atoms. Final coordinates are reported in Tables IV and V.

Acknowledgment. We thank the Consiglio Nazionale delle Richerche and the Ministero della Pubblica Istruzione for financial support and the Centro Interdipartimentale di Metodologie Chimico-fisiche, Università di Napoli, for the use of the WH-270 NMR spectrometer.

Registry No. 1, 15677-39-1; **1a**, 97958-88-8; **1b**, 105991-06-8; **2**, 30834-74-3; **2a**, 105969-48-0; **3**, 110-18-9; **3a**, 105969-52-6; **3b**, 105969-54-8; **4**, 4013-94-9; **4a**, 105991-05-7; **5**, 7032-20-4; **5a**, 105969-53-7; **5b$_c$**, 105969-56-0; **5b$_t$**, 106034-25-7; **6**, 21478-42-2; **6a**, 105969-49-1; **6b**, 105969-55-9; **7**, 105945-18-4; **7a**, 105969-50-4; **7b**, 105969-57-1; **8**, 105945-19-5; **8a**, 105969-51-5; **8b**, 105969-59-3; **9**, 78085-84-4; **9a′**, 97996-49-1; **9a″**, 97958-92-4; **9b**, 105969-58-2; **10**, 106155-16-2; **10a**, 97958-89-9; **11**, 50978-00-2; [PtClMe(C_2H_4)]$_2$, 90523-12-9; C_2H_4, 74-85-1.

Supplementary Material Available: Tables of fractional atomic coordinates for the hydrogen atoms and anisotropic thermal parameters and complete sets of interatomic distances and angles (23 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

---

(28) Sheldrick, G. M. SHELX76, University of Cambridge, Cambridge, 1976.

(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, Great Britain, 1975; Vol. IV, pp 99–149.