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Five-Coordinate Olefin Complexes of Platinum(II) Containing σ-Bonded Carbon Ligands. Coordination Environment and Stability

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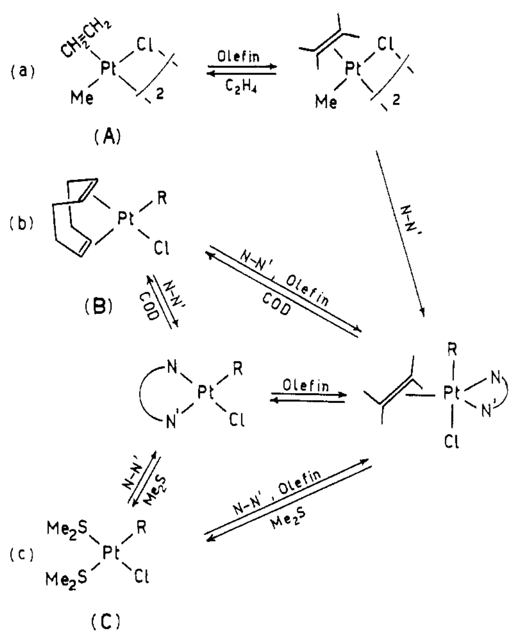
Using three different procedures, trigonal-bipyramidal complexes of the type PtClR(N-N′)(η^2-olefin) have been prepared containing a variety of alkyl or aryl ligands (R), bidentate nitrogen (N-N′), and olefinic ligands. In contrast to other previously known five-coordinate complexes of platinum(II), the dissociation of the olefin from these species is reversible. The equilibria PtClR(N-N′)(olefin) $\overset{K}{\rightleftharpoons}$ PtClR(N-N′) + olefin have been investigated through qualitative observations and through the determination of the dissociation constants by ^{1}H NMR analysis of equilibrium mixtures. The main ligand effects may imply a variation of K_{diss} of several orders of magnitude and are the following: (a) A dominating factor is the steric hindrance present on both sides of the N-N′ ligand. If properly oriented in the coordination plane, this stabilizes the bipyramidal complexes through a corresponding destabilization of the square-planar species. (b) Electron-releasing substituents on the olefinic double bond destabilize the five-coordinate complexes while electron-withdrawing groups stabilize them. This trend is opposite to that observed for square-planar species and provides direct evidence for the relative importance of π-back-donation in five-coordinate Pt(II) olefin complexes.

Introduction

A large number of trigonal-bipyramidal complexes of platinum(II) of general formula PtCl$_2$(N-N)(η^2-olefin), where N-N is a bidentate nitrogen ligand such as a diamine,[1,2] a bis(hydrazone),[3,4] or a diimine,[2b,4-6] have been prepared and characterized during the last decade. The stability of the five-coordinate species was reported to increase with increasing π-acceptor ability of the olefin[4] and donor properties of the nitrogen ligand.[3b-7] It was also markedly affected by the steric requirements of the chelating ligand.[1,2,4,5,7] However, as far as the dissociation of the olefin is involved in the loss of 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 these complexes is reversible. This implies that any attempt to draw a rational correlation between the nature of the ligands and the "stability" of the above-mentioned five-coordinate species will be faced with ill-defined variables such as the mechanism of the olefin dissociation and the structure of the transition state. On the other hand, we recently described the related complexes PtClMe(N-N′)(η^2-C$_2$H$_4$).[8] In these compounds the strong donor methyl group induces the reversible release of the olefin,[8] thus allowing investigation of the factors affecting the thermodynamic stability of five-coordinate species, without the drawback of there being too many uncertain parameters.

Scheme I



In previous reports on this subject,[8,9] it was suggested that an important factor affecting the olefin dissociation equilibrium is the steric bulk present in the coordination plane, on both sides of the bidentate N-N′ ligand. In the case of the all-planar, sp^2-hybridized N-N′ ligand, it was argued that, while the crowding increases, the square-planar species PtClMe(N-N′) are destabilized by the repulsive interaction of the nitrogen substituents with the Cl and Me ligands, resulting in a stabilization of the corresponding trigonal-bipyramidal ethylene complexes. Our investigation so far was limited to complexes of the type PtClMe(N-N′)(η^2-C$_2$H$_4$). As an extension of previous work we synthesized complexes of the type PtClR(η^2-olefin)(N-

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Table I. Selected ^{1}H NMR Data (δ) for Some $PtClR(N\text{-}N')(\eta^2\text{-}C_2H_4)$ and $PtClR(N\text{-}N')$ Complexes[a]

no.	complex	Pt—CH and/or Pt—C—CH	N=CH (iminic)	N—CH or N—CMe (heteroarom)	CH$_2$=CH$_2$
1a$_1$	$PtClMe(2,9\text{-}Me_2\text{-}1,10\text{-}phenanthroline)(C_2H_4)$	−0.07 (71, Me)		3.34 (7)	2.27 (65, d, 2 H),[b] 3.05 (85, d, 2 H)[b]
1$_1$	$PtClMe(2,9\text{-}Me_2\text{-}1,10\text{-}phenanthroline)$	1.37 (79, Me)		2.94 (10), 3.24	
1a$_2$	$PtClEt(2,9\text{-}Me_2\text{-}1,10\text{-}phenanthroline)(C_2H_4)$	0.79 (72, q, 2 H), 0.00 (45, t, 3 H)		3.36 (7)	2.21 (65, d, 2 H),[b] 3.03 (85, d, 2 H)[b]
3a$_3$	PtClPh(quin-2-CH=N-*t*-Bu)(C_2H_4)	6.80 (41, d, 2 H)	9.15 (38)		3.05 (br, 4 H)
3$_3$	PtClPh(quin-2-CH=N-*t*-Bu)	6.96 (40, d, 2 H)	8.95 (34)		
10a$_1$	$PtClMe(6\text{-}Mepy\text{-}2\text{-}CH{=}NC_6H_4OMe)(C_2H_4)$	−0.07 (70, Me)	9.10 (33)	3.10 (5)	2.14 (80, br), 2.30 (80, br), 2.92 (65, br), 3.05 (65, br)
10$_1$	$PtClMe(6\text{-}Mepy\text{-}2\text{-}CH{=}NC_6H_4OMe)$	1.08 (83, Me)	9.24 (94)	3.21	
13a$_1$	$PtClMe(2\text{-}Me\text{-}1,10\text{-}phenanthroline)(C_2H_4)$	0.00 (70, Me)		3.36 (6), 9.51 (18, d)	2.31 (65, m, 2 H), 3.10 (83, m, 2 H)
13$_1$	$PtClMe(2\text{-}Me\text{-}1,10\text{-}phenanthroline)$	1.48 (81, Me)		3.41, 9.45 (64, d)	
14a$_2$	$PtClEt(6\text{-}Mepy\text{-}2\text{-}CH{=}NMe)(C_2H_4)$	0.73 (75, m, 2 H), 0.30 (45, t, 3 H)	8.88 (42)	3.05 (5)	2.03 (65, m, 2 H), 2.85 (86, m, 2 H)
14$_2$	$PtClEt(6\text{-}Mepy\text{-}2\text{-}CH{=}NMe)$	2.20 (88, q, 2 H), 0.93 (45, t, 3 H)			
14a$_4$	$PtCl(4\text{-}MeOC_6H_4)(6\text{-}Mepy\text{-}2\text{-}CH{=}NMe)(C_2H_4)$	6.87 (43, d, 2 H)[b]	8.70 (42)	3.33 (5)	2.4 (br, 1 H), 2.6 (br, 1 H), 3.2 (br, 2 H)
14$_4$	$PtCl(4\text{-}MeOC_6H_4)(6\text{-}Mepy\text{-}2\text{-}CH{=}NMe)$	7.23 (46, d, 2 H)	8.99 (101)	3.19	
16$_3$	PtClPh(6-Hpy-2-CH=N-*t*-Bu)	7.36 (41, d, 2 H)	8.64 (35)	8.43 (59, d)	

[a] 200 or 270 MHz, $CDCl_3$. Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak; no attribute = singlet. Fine structure due to long-range coupling ($J < 2$ Hz) is ignored. Coupling constants to ^{195}Pt are given in parentheses. [b] Pseudodoublets, actually constituting part of a AA′XX′ multiplet.

Table II. Selected ^{1}H NMR Data (δ) for Some $PtClMe(N\text{-}N')(\eta^2\text{-}olefin)$ Complexes[a]

no.	complex	Pt—Me	N—CH or N—CMe (heteroarom)	CH=CH$_2$
1b$_1$	$PtClMe(2,9\text{-}Me_2\text{-}1,10\text{-}phen)(CH_2{=}CHCMe_3)$	0.07 (70)	3.32 (7), 3.49 (7)	2.17 (82, d, 1 H), 2.95 (80, dd, 1 H), 3.41 (76, d, 1 H)
1b$_1$′	as above, rotamer, 45% abundance	0.03 (72)	3.34 (7), 3.58 (7)	2.83 (44, d, 1 H), 3.08 (78, d, 1 H), 4.11 (102, dd, 1 H)
1c$_1$	$PtClMe(2,9\text{-}Me_2\text{-}1,10\text{-}phen)(CH_2{=}CMe_2)$	−0.01 (72)	3.31 (7), 3.40 (7)	2.51 (69, 1 H), 3.33 (87, 1 H)
1d$_1$	$PtClMe(2,9\text{-}Me_2\text{-}1,10\text{-}phen)((E)\text{-}MeCH{=}CHMe)$	−0.08 (72)	3.36 (7), 3.42 (7)	2.77 (58, m, 1 H), 3.62 (94, m, 1 H)
17e$_1$	$PtClMe(6\text{-}Hpy\text{-}2\text{-}CH{=}N\text{-}C_6H_4OMe)((E)\text{-}NCCH{=}CHCN)$	0.60 (66)	9.16 (20, d)	3.08 (63, d, 1 H), 3.97 (82, d, 1 H)
17e$_1$′	as above, diastereom. 15% abundance	0.53 (67)	*b*	2.99 (63, d, 1 H), 4.02 (82, d, 1 H)
21f$_1$	PtClMe(*i*-Pr-N=CHCH=N-*i*-Pr)(maleic anhydr.)	0.28 (67)		4.47 (82, 2 H)
21f$_1$′	as above, rotamer, 35% abundance	0.31 (65)		3.67 (75, 2 H)

[a] 200 or 270 MHz, $CDCl_3$. Abbreviations: d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak; no attribute, singlet. Fine structure due to long range coupling ($J < 2$ Hz) is ignored. Coupling constants to ^{195}Pt are given in parentheses. [b] Signals partially or totally overlapped by those of the former isomer.

N′) (R = alkyl or aryl), having a wide variety of both axial and equatorial ligands, and investigated their olefin dissociation equilibria. We aimed to explore this class of compounds and their properties and to get a more general picture of the influence of the steric and electronic features of the ligands on the stability[10] of the five-coordinate species.[11]

Results and Discussion

General Synthetic Procedures. Three different synthetic procedures have been developed for the preparation of the complexes (Scheme I). Two of these (a and b) were described in our previous paper on $PtClMe(N\text{-}N')(C_2H_4)$ complexes.[8] From procedures b and c only thermodynamically stable complexes[10] can be obtained; however, the starting complexes B and C are more easily handled and stored than A. In procedure c a good compromise is found between stability and reactivity of the starting material, so it is the method of choice in most cases. Since the reactions involved in procedures b and c are actually equilibrium reactions, the monodentate and volatile dimethyl sulfide ligand is easily displaced also by weak N-N′ ligands (such as aromatic imines or hydrazones), which are not usually able to displace cyclooctadiene. The reaction is better performed in diethyl ether, a solvent in which the products generally are less soluble than the reagents. This provides a further driving force and guarantees good yields even in cases where the reaction would be disfavored by a low equilibrium constant. In many cases, the reaction can be performed in two successive steps, the first consisting of isolation of the intermediate four-coordinate $PtClR(N\text{-}N')$ complexes. Procedure c is often preferred, even if complexes C are prepared (when R ≠ Me) from the cyclooctadiene complexes B as shown in eq 1.[12]

$$PtClR(COD) \xrightarrow{80\ ^\circ C,\ Me_2SO} PtClR(Me_2SO)_2 \xrightarrow{Me_2S} PtClR(Me_2S)_2 \quad (1)$$

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[10] Unless otherwise stated, through this paper the terms "stability" and "stable complex" refer to the thermodynamic stability of a five-coordinate complex toward olefin dissociation.

[11] Through this paper we use the following notation: each five-coordinate complex of the type PtClR(N-N′)(olefin) is represented by a sequence of three symbols: a number, indicating the N-N′ ligand, a lower-case letter, indicating the olefin, and a subscript number, indicating the σ-bonded R group. A number or a letter alone indicate a free N-N′ or olefinic ligand, respectively, and a sequence of a number and a subscript number indicates a four-coordinate complex.

Characterization of the Products. The new complexes were characterized through elemental analysis, conductivity measurements (they do not conduct in $CHCl_3$) and ^1H NMR spectroscopy (200 or 270 MHz). Selected ^1H NMR data for part of the complexes are reported in Tables I and II. Table I also reports data for some four-coordinate species. 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 could be unambiguously established for $PtClMe(N\text{-}N')(\eta^2\text{-}C_2H_4)$ complexes has been reported before,[8] and similar arguments are valid in the case of complexes with different olefins or σ-bonded R groups. Some ^{13}C NMR data were also reported in our previous paper.[8] We wish now only to stress that a diagnostic spectral feature[4,6,8] is the large high-field shift of the olefinic protons, compared with the usual range observed for four-coordinate complexes. Typical ethylene chemical shifts (δ) are 5.4 (free ethylene), 4.4–4.8 (four-coordinate complexes),[4,6] 3.3–3.7 (bipyramidal dichloro complexes),[1-7] and 1.7–3.4 (bipyramidal chloro alkyl complexes). We wish also to point out some other relevant spectral features, which can be especially useful for a quick identification of the species present in a mixture of four- and five-coordinate complexes, when it is often difficult to detect and/or assign the signals of the coordinated olefin (e.g. an equilibrium mixture in presence of an excess of free olefin). Some systematic differences between corresponding five- and four-coordinate complexes are the following, as evidenced by inspection of Tables I and II.

(a) If the nitrogen atoms of the N-N′ ligand are sp^2-hybridized, the protons on the σ-bonded carbon in the five-coordinate complex display a chemical shift (δ) about 1 ppm lower than in the four-coordinate complex.

(b) The ^{195}Pt satellite peaks of protons on the σ-bonded carbon in five-coordinate complexes display a $^2J_{H\text{-}Pt}$ coupling constant of about 10 Hz lower than in four-coordinate species ($\sim$70 Hz vs $\sim$80 Hz for methyl derivatives).

(c) In case of iminic ligands the iminic CH proton displays a $^3J_{H\text{-}Pt}$ coupling constant of about 30–40 Hz, while a $^3J_{H\text{-}Pt}$ coupling constant of about 90–100 Hz is observed for four-coordinate complexes, provided the iminic nitrogen is located cis[8,9] to the σ-bonded carbon atom. The latter condition is often not fulfilled, when steric bulk is present on the iminic side of the N-N′ ligand (complexes $\mathbf{15}_1$, $\mathbf{3}_3$, $\mathbf{16}_3$). Indeed, the magnitude of the iminic $^3J_{H\text{-}Pt}$ coupling constant is very useful for establishing the cis or trans configuration for a PtClR(N-N′) complex.[8]

(d) The methyl substituent in 6-methylpyridine-2-caraldimine complexes, as well as in 2-Me-1,10-phenanthroline complexes, exhibits a small $^5J_{H\text{-}Pt}$ coupling constant of 4–7 Hz in five-coordinate species, while no coupling is observed for four-coordinate complexes. The satellite peaks appear as shoulders, broadening the base of the main signal, when a strong magnetic field spectrometer (200 Mz or more) is used, while they appear better resolved in a 60-Mz spectrum.[13]

It is important to note that, whenever olefins other than ethylene are coordinated, different diastereomers can be formed, depending on the symmetry of the olefinic and of the N-N′ ligand. For example, two isomers are possible (and they are actually observed) for the complex $PtClMe(6\text{-}Hpy\text{-}2\text{-}CH{=}NC_6H_4OMe)$(fumarodinitrile) ($\mathbf{17e}_1$), while four isomers are possible (and they are actually observed) for the analogous acrylonitrile complex ($\mathbf{17s}_1$). Since we are mainly concerned here with the synthesis and the stability of the complexes, a discussion of the influence of the ligand environment on the stereochemistry of olefin coordination is beyond the purpose of this work. A detailed investigation on this subject, in progress in our laboratory, will be presented separately.

Olefin Dissociation Equilibria. We have investigated the olefin dissociation equilibria for a number of complexes. These were chosen in order to get informations on the influence of the N-N′ ligand (Chart I), the R ligand (Table III, entries 1–10), and the olefin (Table III, entries 11–33). The dissociation p*K*'s in $CDCl_3$ solution were determined either directly ($pK_{diss} < 3$) or indirectly ($pK_{diss} > 3$). The direct determination was based on the ^1H NMR analysis of an equilibrium mixture of four- and five-coordinate complexes containing an excess of free olefin. Since at least some of the ^1H NMR signals are unambiguously assignable to the four- or to the five-coordinate species (see previous section) and since the olefin exchange rate is very slow on the NMR time scale, integration of the signals gave a direct measure of the relative concentrations. This procedure was not suitable for complexes with low dissociation constants ($pK > 3$), since in these cases the equilibrium concentration of the four-coordinate species was too low to be detected by ^1H NMR with reasonable accuracy. In these cases an olefin exchange reaction, involving a complex with an already known K_{diss}, was used in order to indirectly determine the required dissociation constant. Thus for example the ethylene dissociation constant of complex $\mathbf{10a}_1$ (Table III, entry 22) was determined by ^1H NMR analysis of the olefin exchange equilibrium

$$\underset{\mathbf{10a}_1}{PtClMe(N\text{-}N')(C_2H_4)} + \underset{\mathbf{o}}{CH_2CHCH_2OH} \underset{}{\overset{K}{\rightleftarrows}} \underset{\mathbf{10o}_1}{PtClMe(N\text{-}N')(CH_2CHCH_2OH)} + \underset{\mathbf{a}}{C_2H_4}$$

with the allyl alcohol complex $\mathbf{10o}_1$: $K_{diss}(\mathbf{10a}_1) = KK_{diss}(\mathbf{10o}_1)$.

The time required to reach the equilibrium in the dissociation reactions ranged from a few minutes (e.g. complexes $\mathbf{10a}_1$ and $\mathbf{10g}_1$) to a few days (e.g. complex $\mathbf{1d}_1$).

On the basis of qualitative observations and of the quantitative results reported in Chart I and Table III, we shall now discuss the stability properties of the complexes, as affected by the variation of the N-N′ ligand, the σ-bonded R group, and the olefin.

Variation of the N-N′ Ligand. A number of complexes of the type $PtClMe(N\text{-}N')(\eta^2\text{-}C_2H_4)$ (where N-N′ is a neutral bidentate nitrogen ligand forming a five-membered chelate) have been described in a previous paper.[8] The preparation of other complexes of the same type is reported by this work (see Table I). According to the tendency of the corresponding complex to dissociate the olefin, the N-N′ ligands can be divided in three groups (Chart I): (i) ligands whose five-coordinate complexes do not lose ethylene even under drastic conditions (prolonged boiling in chloroform or other solvents) without extensive decomposition; (ii) ligands for which a five-coordinate ethylene complex is isolable at room temperature, but reversible ethylene dissociation is observable in solution (these are ordered in a sequence matching the decreasing stability order of the corresponding complexes); (iii) ligands whose five-coordinate complexes irreversibly lose ethylene at room temperature.

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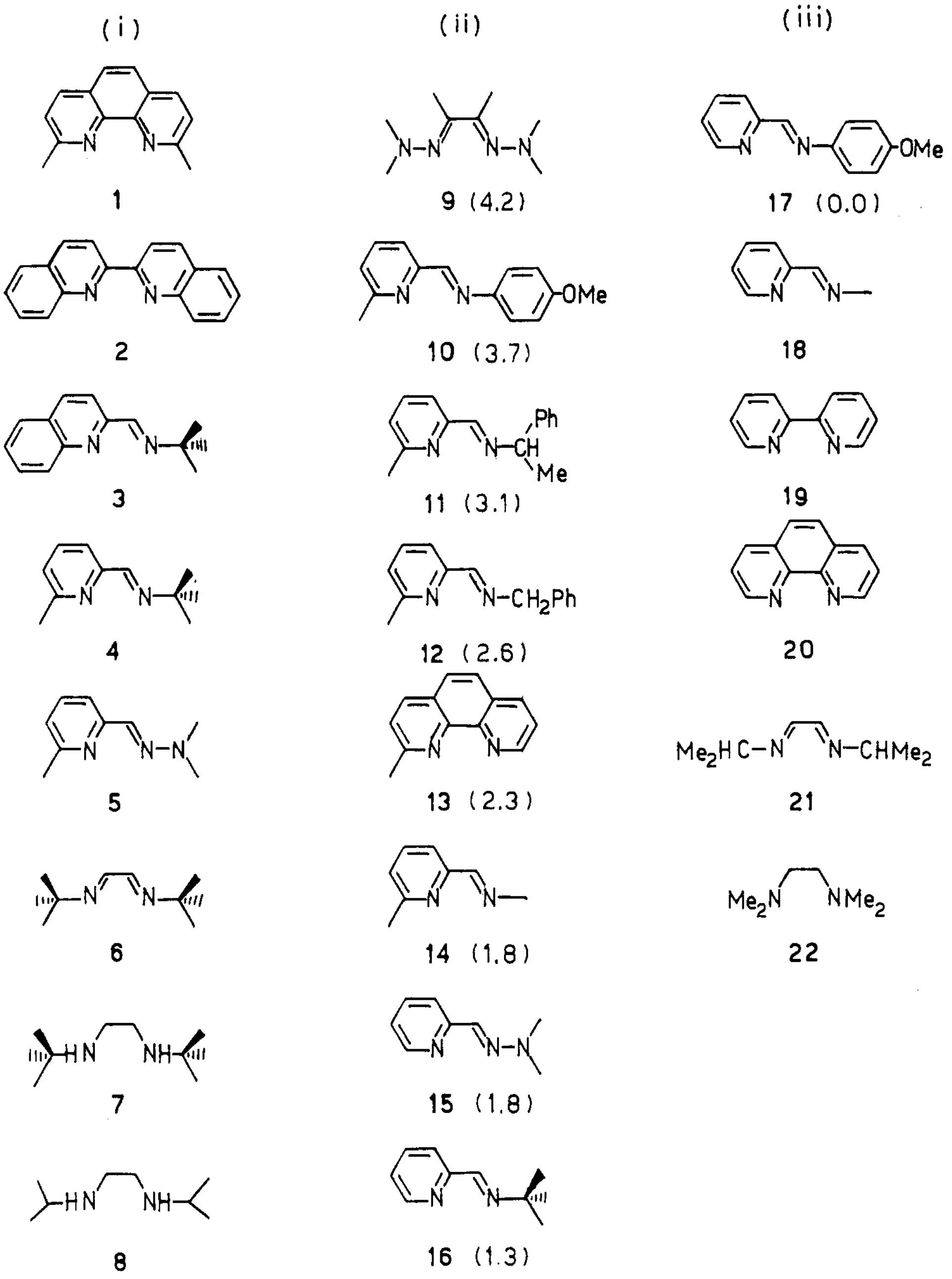
(13) This behavior was observed in similar cases,[7] and can be ascribed to ^{195}Pt chemical shift anisotropic relaxation. See: Lallemand, J. Y.; Soulié, J.; Chottard, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

Chart I. Classification of N-N′ Ligands According to the Stability of PtClMe(N-N′)(C_2H_4) Complexes: (i) No Dissociation Observed; (ii) Reversible Dissociation Observed (pK_{diss} in Parentheses); (iii) Irreversible Dissociation Observed



We want to emphasize that this classification of the N-N′ ligands has to be taken in a *relative* sense. It refers to ethylene complexes. On changing the olefin, five-coordinate complexes can be obtained with group (iii) ligands, provided the appropriate olefin (see later) is used. Likewise, group (i) ligands can give four-coordinate species by dissociation of a five-coordinate complex with a weakly bonded olefin as 3,3-dimethyl-1-butene (**b**) (e.g. complex **1b**$_1$, Table III, entry 25).

By inspection of Chart I, no correlation is apparent between the electronic properties of the N-N′ ligands and the stability of the corresponding five-coordinate complexes. Indeed, both stable and unstable complexes are observed with the good diamine donors, and both stable and unstable complexes are observed with the less good donor pyridine-2-caraldimine and hydrazone ligands. On the other hand, restricting the observation to the planar, sp^2-hybridized N-N′ ligands, a good correlation is found between their steric features and the stability of the corresponding complexes. All group (i) ligands give rise, after chelation, to a structure (iv) where the metal is "embraced" in the coordination plane by carbon substituents protruding toward the ligand(s) on the opposite side. Clearly, as previously suggested,[8] this would give unfavorable interactions with the cis ligands in case of square-planar complexes, while no constraints should be present for the trigonal-bipyramidal species, which are less hindered in the equatorial plane. Accordingly, group (i) ligands selectively stabilize the five-coordinate complexes. When structure (iv) either lacks one "arm" (ligands **13**–**16**) or is

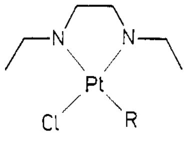


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Table III. Olefin Dissociation Constants (T = 33 °C) for PtClR(N-N′)(olefin) Complexes

entry	compd	N-N′	R	olefin	pK_{diss}
1	**14a**$_1$	6-Mepy-2-CH=NMe	Me	$CH_2=CH_2$	1.8
2	**14a**$_2$		Et		2.3
3	**14a**$_3$		Ph		1.6
4	**14a**$_4$		4-MeOC_6H_4		1.5
5	**10g**$_1$[a]	6-Mepy-2-CH=NC_6H_4OMe	Me	$CH_2=CH-Me$	1.4
6	**10g**$_3$[a]		Ph		1.6
7	**10g**$_4$[a]		4-MeOC_6H_4		1.7
8	**10g**$_5$[a]		4-$CF_3C_6H_4$		1.5
9	**10a**$_6$[a]		2-MeC_6H_4	$CH_2=CH_2$	0.9
10	**10a**$_7$		C_6F_5		0.7
11	**10d**$_1$[a]		Me	(*E*)-MeCH=CHMe	−0.6
12	**10h**$_1$[a]			(*Z*)-MeCH=CHMe	0.2
13	**10i**$_1$[a]			CH_2=CHO-*n*-Bu	0.5
14	**10j**$_1$[a]			CH_2=CHPh	0.7
15	**10k**$_1$[a]			$CH_2=CHC_6F_5$	1.2
16	**10l**$_1$[a]			CH_2=CHEt	1.3
17	**10m**$_1$			$CH_2=CHC(OH)Me_2$	1.7[b]
18	**10n**$_1$[a]			$CH_2=CHCH_2OEt$	2.3
19	**10o**$_1$[a]			$CH_2=CHCH_2OH$	2.8
20	**10p**$_1$[a]			(*E*)-ClCH=CHCl	2.9[b]
21	**10g**$_1$[a]			CH_2=CHCOOMe	3.0[b]
22	**10a**$_1$			$CH_2=CH_2$	3.7
23	**10r**$_1$[a]			CH_2=CHCHO	4.0[b]
24	**10s**$_1$[a]			CH_2=CHCN	5.0
25	**1b**$_1$	2,9-Me_2-1,10-phen		$CH_2=CHCMe_3$	0.4
26	**1d**$_1$			(*E*)-MeCH=CHMe	2.7
27	**17a**$_1$	6-Hpy-2-CH=NC_6H_4OMe		$CH_2=CH_2$	0.0
28	**17s**$_1$[a]			CH_2=CHCN	1.2
29	**17e**$_1$			(*E*)-NCCH=CHCN	3.7
30	**18s**$_1$[a]	6-Hpy-2-CH=NMe		CH_2=CHCN	−0.8
31	**18f**$_1$[a]			maleic anhydr	0.7
32	**19f**$_1$[a]	bipyrid			0.6
33	**19t**$_1$[a]			maleimide	0.2

[a] This complex was not isolated. [b] The ^1H NMR analysis of equilibrium mixtures was made at 60 MHz.

accessible a conformation in which one or both such "arms" are oriented out of the coordination plane (ligands **9**–**12**), the square-planar species become moderately stable, and reversible ethylene dissociation is observed. If structure (iv) lacks both "arms" (ligands **18**–**21**[14]), no steric destabilization of the square-planar species can be present, and, accordingly, the four-coordinate complexes have no tendency to bind ethylene. In case of more flexible, sp^3-hybridized N-N′ ligands such as the diamines **7**, **8**, and **22**, an attempt to rationalize the influence of steric factors on the stability of the five-coordinate complexes has to face more complicated conformational problems. The results obtained with a totally unhindered diamine look rather interesting in this context. When 1,2-ethanediamine was made to react with complex A (see Scheme I) in methylene chloride, a colorless precipitate formed immediately, which on the basis of analytical, conductometric, and NMR evidence (see Experimental Section) could be formulated as the ionic complex $[PtMe(C_2H_4)(H_2NCH_2CH_2NH_2)]Cl$. Also in case of diamines one can thus argue that, in absence of steric constraints that could destabilize a square-planar species, this is the stable form. In the above case, the dissociation of the chloride ion is preferred over the dissociation of the olefin molecule probably as a consequence of the relatively small size of the resulting cation. Within the limited number of diamines investigated, the general trend seems to be that both unhindered diamines and tetrasubstituted ethanediamines for different reasons[15] tend to favor the four-coordinate species, while diamines N-N′-disubstituted with bulky groups (**7**, **8**) favor the five-coordinate complexes.

Variation of the R Ligand. Several complexes of the type PtClR(N-N′)(η^2-C_2H_4) have been prepared and characterized, with a variety of aliphatic and aromatic R ligands, and some of them are listed in Table I. The complexes were prepared starting from the corresponding cyclooctadiene complexes[16,17] PtClR(COD) (B) either directly (preferred for alkyl complexes)[18] or via conversion to dimethyl sulfide complexes (eq 1, preferred for methyl and aryl complexes).

The nature of the R ligand did not critically influence the stability of the five-coordinate species (Table III, entries 1–8); however, two important exceptions are worth mentioning:

First, with N-N′ = 6-Mepy-2-CH=NC_6H_4OMe (**10**) we failed to isolate ethylene complexes in some cases where the R ligand was an ortho-substituted aryl group (a quantitative example is given in Table III, entry 9). In this case, a stability constant of about 3 orders of magnitude lower than for the corresponding phenyl complexes can be estimated.

Second, in case of N-N′ ligands bearing "out of plane" substituents (e.g. *tert*-butylimines), the aryl five-coordinate complexes displayed a substantially lower stability than the methyl complexes. As an example, no five-coordinate species was detectable in saturated ethylene solution ($CDCl_3$) of complex **16**$_3$.[19]

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[14] For ligand **21**, all the methyl groups of the isopropyl substituents are oriented out of the coordination plane in the most stable conformation of the complex.[9]

[15] In five-coordinate complexes of tetrasubstituted ethanediamines, a steric interaction between the substituents on the nitrogen atoms and the axial ligand(s) can be responsible of the observed instability.

[16] Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105.

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

[18] For alkyl complexes, the conversion of the cyclooctadiene complex B to the dimethyl sulfide complex C is not convenient because of decomposition occurring during the first step (see eq 1).

[19] Five-coordinate species were detectable by adding to **16**$_3$ electron-withdrawing olefins such as acrylonitrile and maleimide.

Both the above observations can be rationalized in terms of a destabilization of the bipyramidal species by steric interaction between the axial and equatorial ligands. In the first case this would involve the ortho substituent on the benzene ring and one or more of the atoms of the ligands in the equatorial plane. Indeed, such interaction is *not* present in the square-planar complexes, since the aromatic ring is expected to be nearly orthogonal to the coordination plane.[20] In the second case the equatorial–axial interaction would involve the benzene ring and an "out of plane" methyl group of the *tert*-butyl substituent. This would be negligible in case of a relatively small axial ligand as the methyl group. It is worth noting that similar axial–equatorial interactions could explain the observed instability of five-coordinate complexes with tetrasubstituted ethanediamines.[15]

Looking at minor effects, the slight decrease in pK_{diss} going from R = 4-MeOC$_6$H$_4$ to R = 4-CF$_3$C$_6$H$_4$ (Table III, entries 7 and 8) suggests that the stability of a five-coordinate species increases with the donor power of the R ligand. This effect can contribute to the good stability of the ethyl complex **14a**$_2$ compared with the methyl complex **14a**$_1$ (Table III, entries 1 and 2) and to the low stability of the pentafluorophenyl complex **10a**$_7$ (Table III, entry 10). However, in the latter case the observed instability of the five-coordinate species is probably mainly due to the double ortho substitution of the aromatic ring (see for comparison Table III, entry 9).

The results reported in this and in the previous section indicate that within the range of N-N′ and R ligands investigated, electronic factors influence the stability of five-coordinate olefin complexes in only a minor way; steric factors dominate. A substantial "nonsteric" effect on the stability of bipyramidal species would require a drastic change in the ancillary ligands, probably involving the nature of the donor atoms.

Variation of the Olefin. Complexes of the type PtClR(N-N′)(olefin) with alkenes different from ethylene can be obtained either by using the appropriate olefin in the procedures described in Scheme I or by exchanging ethylene in the already formed five-coordinate complex. We found the former approach to be more generally applicable, since it can be used with olefins that give much less stable complexes than ethylene (see later) and with some group (i) ligands, like **1**, whose ethylene complexes display a very slow olefin exchange rate. The title complexes can be obtained with a large variety of alkenes, with the possible exception of trisubstituted and other sterically hindered olefins. A selection of the complexes that have been prepared and their ^{1}H NMR data is reported in Table II.

The nature of the double-bond substituents has a remarkable effect on the stability of the five-coordinate species. Compared with ethylene, olefins bearing electron-releasing substituents give generally less stable complexes and olefins bearing electron-withdrawing substituents give complexes of comparable or greater stability. When purely hydrocarbon olefins other than ethylene are used, stable complexes can be obtained only with group (i) ligands and in some cases with the two upper ligands in group (ii). Conversely, in case of olefins bearing electron-withdrawing substituents, stable complexes can be obtained with all group (i) and (ii) ligands and can be at least detected even with most group (iii) ligands. For example, in order to isolate stable (*E*)-2-butene complexes, ligands like **1** or **3** had to be used. On the other hand, five-coordinate complexes were formed with maleic anhydride even in the presence of ligands such as 6-Hpy-2-CH=NMe (**18**) and bipyridine (**19**). A quantitative illustration of the affinity of the same PtClR(N-N′) moiety toward different olefins is given in Table III, entries 11–24. These entries are ordered in a sequence of increasing stability of the five-coordinate complexes. The ethylene (**a**) and acrylonitrile (**s**) dissociation constants have been measured for a couple of PtClMe(N-N′) fragments containing different N-N′ ligands (Table III, entries 22, 24, 27, and 28). The difference in pK_{diss} values for the two olefins is 1.3 for ligand **10** and 1.2 for ligand **17**, thus being nearly independent on the N-N′ ligand. This also means that the difference in pK_{diss} values for the two N-N′ ligands is nearly independent on the olefin. Although this conclusion has been verified in a single case, it seems reasonable to assume it is generally valid, at least at a semiquantitative level. As a consequence, combining different results in Table III, an approximate prediction can be made, concerning a complex whose pK_{diss} has not been (or cannot be) experimentally determined. Thus for example, combining the results in Table III, entries 11, 22, and 26, it is possible to estimate a pK_{diss} value of about 7 for the complex PtClMe(2,9-Me$_2$-1,10-phenanthroline)(C$_2$H$_4$) (**1a**$_1$). Again, combining the pK_{diss} values in entries 22, 24, and 30, it is possible to estimate a pK_{diss} value of about −2 for the complex PtClMe(6-Hpy-2-CH=N-Me)(C$_2$H$_4$) (**18a**$_1$).

Although it is generally not possible to completely discriminate between steric and electronic effects, such effects are qualitatively apparent from the pK_{diss} values reported in Table III. The stability of a five-coordinate complex increases on reducing the steric hindrance of the olefin (as intuitively expected) and increasing the electron-withdrawing ability of the substituents and vice-versa.[21] Taking the ethylene complex as a reference, such effects act in the same direction when olefins bearing electron-releasing substituents are used, while they act in opposite directions when electron-withdrawing substituents are introduced. If complexes with monosubstituted olefins are considered, a very low value in the stability scale is thus reached with 3,3-dimethyl-1-butene (**b**), which combines a large steric hindrance with a relatively high electron-releasing ability of the *tert*-butyl substituent. On the opposite side is acrylonitrile (**s**), which combines a minimum steric hindrance with the high electron-withdrawing power of the C≡N substituent.

It is interesting at this point to make a comparison with the behavior of the usual four-coordinate Pt(II) olefin complexes. The paucity of literature data concerning square-planar complexes of electron-withdrawing olefins[22] suggests a low stability for these species, and this trend is confirmed by the results of quantitative thermodynamic investigations.[23] In addition, during this work we have observed by ^{1}H NMR that addition of a moderate excess

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[20] See, for example: Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevuto, V.; Romeo, R.; Belluco, U. *Inorg. Chim. Acta* **1978**, *31*, 171.

[21] The presence of electron-releasing substituents on the double bond was previously shown to destabilize the five-coordination in PtCl$_2$(N-N′)(olefin) complexes, by favoring the dissociation of one tooth of a bidentate diiminic ligand.[4]

[22] No four-coordinate Pt(II) complex of olefins bearing electron-withdrawing substituents is quoted in *Dictionary of Organometallic Compounds*, 2nd Supplement; Chapman and Hall; London, New York, Toronto, 1986. Two rare examples are a methyl acrylate complex that was claimed in 1977 to be the first in this class (Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1977**, *21*, 251) and an ethyl α-chloroacrylate complex that was previously reported by one of us (Panunzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1966**, *88*, 4843).

[23] (a) Kurosawa, H.; Asada, N. *J. Organomet. Chem.* **1981**, *217*, 259. (b) Kurosawa, H.; Urabe, A.; Emoto, M. *J. Chem. Soc., Dalton Trans.* **1986**, 891.

(2 equiv in 0.1 M $CDCl_3$ solution) of an hydrocarbon olefin such as 1-pentene or 1-hexene to the complex $[PtClMe(C_2H_4)]_2$ (A) results in a fast-exchange equilibrium, with partial ethylene displacement. In contrast, electron-withdrawing olefins such as maleimide or dimethylfumarate do not displace ethylene under the same conditions.

The electronic effect of the olefinic substituents is thus opposite in five- and four-coordinate complexes. Whatever the contribution of π-back-donation to the platinum–olefin bond in four-coordinate complexes might be, the above observations provide direct chemical evidence that this contribution is of much greater importance for five- than four-coordinate species. Previous suggestions on this point, mainly based on NMR spectroscopic properties,[8,24] are thus substantiated.

Conclusions

The results we have reported show that a moderately wide variation of the ligands is achievable within the class of compounds represented by the title complexes. After a qualitative and quantitative examination of the relative stability of the complexes, at least two points appear now to be clear:

(a) In the case of planar N-N′ ligands, the stability of the five-coordinate species strictly depends on the capacity of the ligand to destabilize the corresponding square-planar species through interligand steric interactions in the coordination plane. Electronic effects due to a moderate variation of the donor ability of the nitrogen or R ligand have a minor influence.

(b) The presence of electron-withdrawing substituents on the double bond tends to increase the stability of the five-coordinate species, while the opposite effect has been observed for four-coordinate Pt(II) olefin complexes. This is direct evidence that, as one might expect intuitively, coordinative saturation at a metal center greatly increases its ability to back-donate π-electron density.

In addition to the above conclusions, it must be stated that in presence of bulky R ligands and/or N-N′ ligands bearing "out of plane" substituents, equatorial–axial steric interactions can destabilize five-coordinate species.

Finally, it now seems possible to "modulate" the stability of a five-coordinate complex through an appropriate choice of the olefinic and N-N′ ligands. In other words, once an olefin is chosen, in most cases it should be possible to find a N-N′ ligand such that a complex within a given range of stability can be formed. For a given olefin, the stability constant that can be obtained by varying the N-N′ ligand spans a range of at least 9 orders of magnitude. Likewise, for a given N-N′ ligand, the variation of stability constant obtained by varying the olefin spans a range of more than 9 orders of magnitude.

Experimental Section

^1H NMR spectra were recorded at 60 MHz on a Varian T-60 A spectrometer and at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. Unless otherwise stated, $CDCl_3$ was used as solvent and TMS as internal standard.

Solvents and reagents were of AnalaR grade, unless otherwise stated, and 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. Ligands **1**, **2**, **19**, and **20** are commercially available; **7**[1a] and **13**[25] were prepared as previously described; **3**, **5**, **10**, **15**, and **17** were prepared by 1:1 molar ratio condensation of the appropriate aldehyde and primary amine (or hydrazine).[7] For the other N-N′ ligands see ref 8 and references therein. **$[PtClMe(C_2H_4)]_2$**[26] and **$PtClMe(Me_2S)_2$**[27] were prepared as previously reported and were handled and stored under nitrogen. **$PtEt_2(COD)$**,[17] **$Pt(n\text{-}Pr)_2(COD)$**,[17] **$Pt(i\text{-}Pr)_2(COD)$**,[28] **$Pt(CH_2CMe_3)_2(COD)$**,[29] **$PtPh_2(COD)$**,[17] **$Pt(4\text{-}MeO\text{-}C_6H_4)_2(COD)$**,[30] **$Pt(3\text{-}MeO\text{-}C_6H_4)_2(COD)$**,[30] **$Pt(4\text{-}CF_3\text{-}C_6H_4)_2(COD)$**,[30] **$Pt(4\text{-}F\text{-}C_6H_4)_2(COD)$**,[16] **$Pt(2\text{-}Me\text{-}C_6H_4)_2(COD)$**,[16] and **$PtCl(C_6F_5)(COD)$**[31] were prepared as previously described. The dialkyl (diaryl) complexes were converted to the corresponding monoalkyl (monoaryl) chloro complexes following a previously reported procedure.[17] **$PtClR(Me_2S)_2$** complexes were prepared according to eq 1.[12]

Synthesis of $PtClMe(N\text{-}N')(\eta^2\text{-olefin})$ Complexes from $[PtClMe(C_2H_4)]_2$. Ethylene complexes were prepared as previously described.[8] Complexes with olefins not bearing electron-withdrawing substituents were prepared by using the following procedure: 275 mg (0.5 mmol) of $[PtClMe(C_2H_4)]_2$ (A) was dissolved in 4 mL of methylene chloride at 0 °C, and a large excess (1 mL) of the appropriate liquid olefin was added. The solution was evaporated in vacuo at 0 °C, the residue was immediately suspended (partially dissolved) in anhydrous diethyl ether (3 mL), and 1.1 mmol of the appropriate N-N′ ligand was added under stirring at 0 °C. A colorless to yellow precipitate formed, which after 30 min of stirring was collected on a filter and dried, giving the required PtClMe(N-N′)(olefin) complex in 75–90% yield. In case of thermodynamically unstable complexes (e.g. **17a**$_1$, **19a**$_1$, **20a**$_1$) the addition of the N-N′ ligand and all the successive operations were performed at −30 °C.

Synthesis of $PtClR(N\text{-}N')(\eta^2\text{-olefin})$ Complexes from PtClR(COD). The following procedure was used only for the preparation of ethyl and higher alkyl derivatives. For the reasons already discussed, in case of methyl and aryl complexes it was more convenient to use the next procedure, starting from $PtClR(Me_2S)_2$. To a chloroform solution (0.3 mmol/mL) of the cyclooctadiene complex PtClR(COD) was added an excess (2 eq) of the appropriate N-N′ ligand, and the solution was stirred under ethylene pressure (3 atm) for 48 h at room temperature (for complexes of other alkenes, a large excess of the olefin was used). By addition of diethyl ether, the required crude complex was obtained in 70–90% yield as a yellow solid. The complexes could be recrystallized from methylene chloride–diethyl ether.

Synthesis of $PtClR(N\text{-}N')(\eta^2\text{-olefin})$ Complexes from $PtClR(Me_2S)_2$. To a solution/suspension of 1.0 mmol of the dimethyl sulfide complex $PtClR(Me_2S)_2$ in 20 mL of diethyl ether was added a 30% molar excess of the appropriate N-N′ ligand, and the mixture was stirred under ethylene at atmospheric pressure for 15 h at room temperature (for complexes of liquid olefins, 0.5 mL of the olefin were used, while a 50% molar excess was used in case of solid olefins). The resulting colorless to yellow precipitate was collected on a filter and dried, giving the required complex in 70–90% yield. The complexes could be recrystallized from methylene chloride–diethyl ether.

Synthesis of $PtClR(N\text{-}N')$ Complexes from $PtClR(Me_2S)_2$. To a solution/suspension of 1.0 mmol of the dimethyl sulfide complex $PtClR(Me_2S)_2$ in 20 mL of diethyl ether was added a 30% molar excess of the appropriate N-N′ ligand, and the mixture was stirred at room temperature for 6 h. The solvent was evaporated in order to remove any free dimethyl sulfide, 20 mL of diethyl ether was added to the residue, the mixture was stirred for further 6 h, and this procedure was repeated once. Finally, after evaporation of the solvent, the residue was crystallized from methylene chloride–diethyl ether, giving the required complex in 65–90% yield. Alternatively, the complexes could be prepared by repeatedly (2–4 times) boiling to dryness a chloroform solution

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of the corresponding PtClR(N-N′)(C_2H_4) complex (ligands from **9** to **16**) or PtClR(N-N′)((*E*)-2-butene) (ligands **1** and **3**). For particularly resistant five-coordinate complexes (e.g. **1d**$_1$, **3a**$_3$), a small amount of tetrachloroethane was added to the solution, in order to increase the boiling point, and the solution was repeatedly evaporated at 100 °C to almost dryness.

Synthesis and Characterization of [PtMe($H_2NCH_2CH_2NH_2$)(C_2H_4)]Cl. Complex A (137 mg, 0.25 mmol) was dissolved in 4 mL of methylene chloride at 0 °C, and 35 μL (0.52 mmol) of ethanediamine were added to the solution. After a few seconds a colorless microcrystalline solid precipitated, which was collected on a filter, washed with methylene chloride, and dried (yield 150 mg, 90%). This compound is not soluble in methylene chloride and chloroform, slightly soluble in methanol, and soluble in water. The methanol solution displays a molar conductivity of about 80 $\Omega^{-1}\cdot mol^{-1}\cdot cm^2$ ($c = 5 \times 10^{-3}$ mol/L). Anal. Calcd for $C_5H_{15}ClN_2Pt$: C, 18.00; H, 4.53; Cl, 10.62; N, 8.39. Found: C, 17.51; H, 4.56; Cl, 11.03; N, 8.31. ^{1}H NMR (δ in D_2O): 0.30 (s, Pt–Me, $^2J_{H\text{-}Pt}$ = 75 Hz), 2.92 (m, 2 H, $^3J_{H\text{-}Pt}$ = 15 Hz), 3.10 (m, 2 H, $^3J_{H\text{-}Pt}$ = 45 Hz), 4.05 (br s, $CH_2{=}CH_2$, no coupling to ^{195}Pt detected). No significant changes in the ^{1}H NMR spectrum of the compound were observed after treatment of the D_2O solution with $AgBF_4$ and removing the resulting AgCl precipitate.

Determination of the Equilibrium Constants of the Olefin Dissociation Reactions. The equilibrium constants were determined by ^{1}H NMR analysis of equilibrium mixtures at 33 °C. This temperature was chosen because the measurements were initially made on a Varian T-60 A spectrometer at the constant probe temperature of 33 °C. For consistence of data, the same temperature was kept in all the successive measurements, recorded on other spectrometers equipped with variable-temperature probes (Varian XL-200 or Bruker AC-270). In case the five-coordinate complex PtClR(N-N′)(olefin) had been previously isolated, this was initially used in the experiment; otherwise the parent four-coordinate complex PtClR(N-N′) was used instead.

A weighed amount of the complex (3–20 mg, depending on the solubility) was dissolved in 0.600 mL of $CDCl_3$ in a gas-tight NMR tube. Some free olefin was then added, and the solution was kept at 33 °C until no more change in the ^{1}H NMR spectrum was observed. The relative concentrations of the free olefin and of the four- and five-coordinate species were then measured by integration of the corresponding signals, allowing the evaluation of the equilibrium constant. In case of isomeric mixtures of five-coordinate species, a global constant was calculated, involving the sum of the concentrations of the various detectable isomers. For each compound at least two independent solutions were prepared at a different metal concentration, and for each of these, at least three different measurements were made at a different olefin concentration. The p*K*'s values reported in Chart I and Table III are the average of the values calculated from each measurements. The estimated average error is less than 0.1 logarithmic units for p*K*'s values between 1 and 2 but can be larger outside this interval. The equilibrium constants of olefin exchange reactions, involved in the indirect determination of dissociation constants, were similarly determined: two different olefins were added to a solution of the same complex and the relative concentrations of the different five-coordinate complexes were measured by integration of the corresponding signals.

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Registry No. **1**$_1$, 119743-70-3; **1a**$_1$, 119743-69-0; **1a**$_2$, 119769-35-6; **1a**$_4$, 119743-84-9; **1a**$_8$, 119743-85-0; **1a**$_9$, 119744-40-0; **1a**$_{10}$, 119743-86-1; **1b**$_1$, 119744-11-5; **1b**$_4'$, 119816-18-1; **1c**$_1$, 119769-36-7; **1d**$_1$, 119744-12-6; **1g**$_1$, 119744-13-7; **1g**$_1'$, 119816-19-2; **1h**$_1$, 119816-20-5; **1h**$_1'$, 119816-21-6; **2a**$_1$, 119743-78-1; **2a**$_2$, 119743-87-2; **2a**$_{10}$, 119743-88-3; **3**$_3$, 119743-90-7; **3a**$_1$, 119743-79-2; **3a**$_3$, 119743-89-4; **3d**$_1$, 119744-14-8; **3d**$_1'$, 119816-22-7; **4u**$_1$, 119744-15-9; **5a**$_1$, 119743-80-5; **7a**$_1$, 119743-81-6; **10**$_1$, 119743-76-9; **10**$_3$, 119743-93-0; **10**$_4$, 119743-95-2; **10**$_5$, 119743-95-2; **10**$_6$, 119744-09-1; **10**$_7$, 119743-99-6; **10**$_{11}$, 119744-41-1; **10**$_{12}$, 119744-02-4; **10a**$_1$, 119743-82-7; **10a**$_2$, 119743-91-8; **10a**$_3$, 119743-92-9; **10a**$_4$, 119743-94-1; **10a**$_5$, 119743-96-3; **10a**$_7$, 119743-98-5; **10a**$_{11}$, 119744-00-2; **10a**$_{12}$, 119744-01-3; **10d**$_1$, 119744-24-0; **10g**$_1$, 119744-20-6; **10g**$_3$, 119744-21-7; **10g**$_4$, 119744-22-8; **10g**$_5$, 119744-23-9; **10h**$_1$, 119816-25-0; **10i**$_1$, 119744-25-1; **10j**$_1$, 119744-26-2; **10k**$_1$, 119744-27-3; **10l**$_1$, 119744-28-4; **10m**$_1$, 119744-16-0; **10n**$_1$, 119744-29-5; **10o**$_1$, 119744-30-8; **10p**$_1$, 119744-31-9; **10q**$_1$, 119744-32-0; **10r**$_1$, 119744-33-1; **10s**$_1$, 119744-34-2; **13**$_1$, 119743-72-5; **13a**$_1$, 119743-71-4; **14**$_2$, 119744-04-6; **14**$_3$, 119744-06-8; **14**$_4$, 119744-08-0; **14a**$_1$, 105969-50-4; **14a**$_2$, 119744-03-5; **14a**$_3$, 119744-05-7; **14a**$_4$, 119744-07-9; **14p**$_1$, 119744-17-1; **15**$_1$, 119743-74-7; **15a**$_1$, 119743-73-6; **16**$_3$, 119744-10-4; **17**$_1$, 119743-76-9; **17a**$_1$, 119743-75-8; **17e**$_1$, 119744-18-2; **17e**$_1'$, 119816-23-8; **17s**$_1$, 119744-35-3; **18f**$_1$, 119744-37-5; **18s**$_1$, 119744-36-4; **19a**$_1$, 119743-77-0; **19f**$_1$, 119744-38-6; **19t**$_1$, 119744-39-7; **20a**$_1$, 119743-83-8; **21f**$_1$, 119744-19-3; **21f**$_1'$, 119816-24-9; A, 90523-12-9; C (R = Me), 87145-39-9; [PtMe($H_2NCH_2CH_2NH_2$)(C_2H_4)]Cl, 119743-68-9; $PtEt_2$(COD), 51192-20-2; Pt(*n*-Pr)$_2$(COD), 113451-83-5; Pt(*i*-Pr)$_2$(COD), 12130-04-0; Pt(CH_2CMe_3)$_2$(COD), 75101-19-8; $PtPh_2$(COD), 12277-88-2; Pt(4-MeO-C_6H_4)$_2$(COD), 54866-09-0; Pt(3-MeO-C_6H_4)$_2$(COD), 57110-65-3; Pt(4-CF_3-C_6H_4)$_2$(COD), 90478-98-1; Pt(4-F-C_6H_4)$_2$(COD), 54866-13-6; Pt(2-Me-C_6H_4)$_2$(COD), 54866-12-5; PtCl(C_6F_5)(COD), 112084-27-2.

Supplementary Material Available: ^{1}H NMR data for all the new complexes (Tables S1–S4) and analytical data (Table S5) (10 pages). Ordering informaton is given on any current masthead page.